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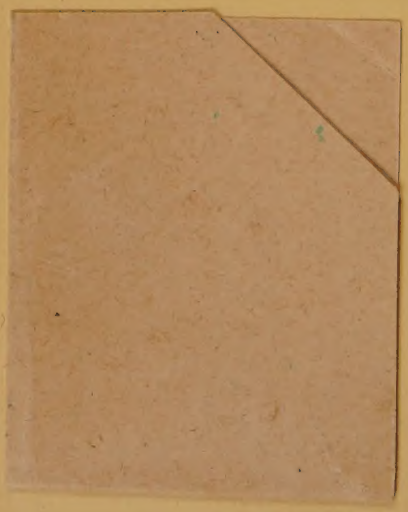

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THE SCIENTIFIC EXAMINATION OF PICTURES

THE SCIENTIFIC EXAMINATION OF PICTURES

AN INVESTIGATION OF THE PIGMENTS USED BY THE DUTCH AND FLEMISH MASTERS FROM THE BROTHERS VAN EYCK TO THE MIDDLE OF THE 19TH CENTURY

BY

DR. A. MARTIN DE WILD

WITH A FOREWORD BY

PROF. DR. F. E. C. SCHEFFER

Professor of Inorganic Chemistry at the Technical University of Delft, Holland

---

TRANSLATED FROM THE DUTCH BY

L. C. JACKSON, M.Sc., Ph.D. (Leiden)

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FOREWORD

During the last few years I have been repeatedly asked to determine whether a particular picture is genuine or not. Although this question, put in this form, certainly cannot be answered in every case by a trained chemist, I have found that a definite answer is possible in by far the greater number of cases put before me for a decision. When it is a question whether a particular painting is really the work of a painter of, for example, the Dutch School of the 17th century or whether it is a modern imitation, the answer can nearly always be given with complete certainty by a chemical investigation. The facts which make such a conclusion possible are to be found not only in the different behaviour of paint-layers of different ages with respect to physical or chemical action, but also in the nature of the substances used in the paintings.

In these investigations, which I carried out in collaboration with Dr. A. Martin de Wild, an ex-student of the Technical University of Delft, the lack of sufficient information as to the nature of the pigments used in oil-painting during the period under review made itself felt. Important conclusions are indeed to be drawn from the dates of the discovery of various synthetic pigments which can be found in chemical literature, and on this subject something can be learnt from recipes in the old books on painting; but the first-mentioned source

is only to a limited extent at our disposal—the oldest information dates from the 18th century—and the books on painting, written at a time when chemistry was only developed to a very small degree, naturally do not always give complete certainty as to the chemical character of the pigments used.

For our investigations this lack was partially met by the Inorganic Chemical Laboratory of the Technical University of Delft (thanks to the kindness of Mr. J. Nolet) coming into possession of a collection of pigments made by a member of the firm of Hafkenscheid of Amsterdam at the beginning of the 19th century, but this still only furnished a partial solution of the difficulty.

Dr. A. Martin de Wild undertook, for the purpose of preparing a thesis to be presented at the Technical University, to investigate the pigments which occur in paintings of various ages. It goes without saying that in order to obtain trustworthy results it was absolutely necessary to experiment on pictures whose origin was above suspicion. It was fortunate from this point of view that Dr. de Wild, besides his training at the Technical University, had passed through an excellent school in the studio of his father, Mr. D. de Wild, who is well known not only in Holland but also in England and America as a restorer of pictures. The fact that, during a case which was heard in 1924–1925 before the Court at the Hague, I was able to show that the possession of certain data concerning the pigments used in former times was of the greatest importance in determining

with certainty the age of a picture, was probably also a help in obtaining the necessary permissions.

Dr. de Wild was then able to obtain permission from numerous authorities and governing bodies, the possessors of pictures above suspicion, to take small specimens of paint from pictures of very diverse ages for the purpose of his researches. How this sampling has been carried out without danger or damage to the paintings, the reader will find described in this work by Dr. de Wild. We may here mention with thanks the aid of the following authorities and governing bodies:

Prof. Dr. W. Martin, Director of the Royal Picture Gallery (Mauritshuis) at the Hague, and Dr. H. Schneider, Assistant at the same museum, gave Dr. de Wild aid and information in connection with taking specimens from paintings in the depôt of the above-mentioned gallery, for which purpose His Excellency the Minister of Education, Arts and Sciences had given permission.

Mr. Schmidt Degener, Chief Director of the Rijksmuseum at Amsterdam, and the Hon. D. C. Roëll did the same for the depôt of the latter museum.

The Corporation of Haarlem gave access to the Frans Hals Museum, where the Director, Mr. G. D. Gratama, continually showed his interest.

The Corporation of the Hague gave access to the Municipal Museum, where Dr. H. E. van Gelder, Director of the Service of Arts and Sciences, and Dr. G. Knuttel, Conservator of the Municipal Museums, gave their assistance.

Dr. W. S. Unger gave similar help in connection with a picture from the Municipal Museum at Middelburg.

Some specimens of ancient Egyptian paint were obtained for comparison from the Museum of Antiquities of Leiden, thanks to the kindness of the Director, Dr. J. H. Holwerda, and the Conservator, Dr. W. D. van Wijngaarden.

We are also grateful to Dr. A. H. Cornette, Director of the Royal Museum of Fine Arts at Antwerp, where data of the greatest value were collected concerning the Flemish Primitive School. Mr. J. Muls also gave valuable help here.

Mr. James L. Caw and Mr. Stanley Cursiter, both of the National Gallery of Scotland at Edinburgh, gave Dr. de Wild their kind assistance during his investigation of the state of preservation of the Dutch paintings there.

Dr. de Wild has systematically arranged about 300 data relating to a period from 1430, practically, that is, from the beginning of oil-technique up to the present time, and has collected them into a table which summarises the results of the investigation.

Although the methods of determining the age of pictures mentioned at the beginning are not themselves treated in this work, Dr. de Wild has found space to include some interesting results obtained from an examination by means of X-rays. He has chosen some of the most striking examples for this purpose, among which the discovery of the

Frans Hals in the gallery at Edinburgh will no doubt attract great attention.

His chapter on the preservation of paintings comes with the authority of one who is himself engaged in the work.

I trust, then, that the present volume will find a place of its own. Dr. de Wild will naturally much appreciate comments on his work, which may be addressed to him c/o the Technical University, Delft, Holland.

F. E. C. SCHEFFER

DELFT, *January* 1929.

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CHAPTER I

HISTORICAL AND SCIENTIFIC INVESTIGATION

The guiding thought in the study of old pictures from the point of view of the history of art will in general be formed by the impression which the representation produces.

It is the idea or conception which speaks directly to the beholder, quite apart from the object with which he examines the painting.

The line of thought of the producer embodied in the picture is the immediate cause of the formation of a more or less corresponding line of thought in the mind of the beholder.

The impressions produced by any given representation will be various. They will first of all concern the action, the scene or the person which is reproduced in the picture. Afterwards interest will be aroused in the manner in which the delineation of that action, scene or person has been carried out; for example, whether it corresponds to the reality.

Further, the colour, the drawing, the general construction, and finally the details of the brushwork can furnish important information.

The combination of all these and often many other data leads to a final conclusion, from which one can assign the picture to a definite producer, a definite school, a definite period or a definite place of origin. On the other hand, a more general study of the old pictures will furnish important information concerning the state of development and culture then prevailing. The manner of the delineation will

frequently speak more clearly on this topic than old literature can ever do.

It is obvious that the purely subjective judgement plays a prominent part in this manner of studying old pictures, and therein lies the explanation of the fact that the final conclusions concerning one and the same work of art can exhibit very great differences among themselves without its being in the least necessary on that account to reject any one of them; for each may contain valuable matter for further investigation.

The data concerning the material construction of old paintings are very meagre compared with the very large amount of material which the study of them from the point of view of the history of art has brought together during the course of years. Although it is not to be expected that the study of the materials can lead to conclusions of such profound importance concerning the origin of a picture as can the history of art, its results will be able to bring about an enlargement of historical opinions and scientific investigation can lead to a decision in doubtful cases.

The question now arises, In what way can the facts of the material construction of the old paintings be collected?

First of all the pictures themselves must be considered for this purpose. Provided that their origin is above suspicion, they acquaint us in an unambiguous manner with the paints, the primings and the mediums which were employed. These data, furthermore, furnish an insight into the permanency of the old paintings, the causes of their decay, and their

present state of preservation, and they lead at the same time to the methods by which that present state may be conserved or improved. Next, the old technical books on painting may be studied with advantage. Finally, the history of chemistry, especially with regard to the epoch of the discovery or commercial preparation of new pigments, will be of great value.

Only a few data have been collected in the literature concerning the first point, the investigation of the pigments used in old paintings. The researches of Raehlmann,[1] which were carried out at the beginning of this century, include the microscopic investigation of a number of pigments. In this he laid emphasis principally on the external forms, as a result of which the importance of microchemical confirmation did not always come equally sharply into prominence. He brought together data concerning the technique of a large number of works of art, mainly of Italian origin. His study of the production of colour effects by the application of differently coloured layers superimposed on one another is especially important. It is, however, to be regretted that the origin of the pictures he studied is not indicated in any way.

Similar investigations have also been carried out by Laurie.[2] He has principally collected references in the old literature to the use of various pigments. In addition he records microchemical reactions on pigments, and has applied these to a few pictures His work is, however, for the most part concerned

[1] *Über die Maltechnik der Alten mit besonderer Berücksichtigung der Römisch-Pompejanischen Wandmalerei*, Berlin, 1910; *Über die Farbstoffe der Malerei in den verschiedenen Kunstperioden nach mikroskopischen Untersuchungen*, Leipzig, 1914.

[2] *The Pigments and Mediums of the Old Masters*, 1914.

with the so-called "illumination", for which purpose he has studied various old manuscripts.

As concerns the old technical recipes for painting, which are provided by Dutch literature of the 17th century, it may be remarked that the writers have generally contented themselves with an enumeration of the pigments employed, whilst sometimes in addition an accurate description is given of those pigments with which a particular object can be painted. It is only very seldom that anything is recorded concerning the preparation of the pigments. The so-called *Secreet-Boeck* (*Secret Book*),[1] which, as far as I know, is the only original Dutch work giving extensive recipes for the preparation of a number of pigments and binding-media, forms an exception to this rule. Since this document is very scarce and hence not easily accessible, some of these recipes are reproduced word for word in the following pages.

The information derived from the history of chemistry dates for the greater part from the end of the 18th century and the beginning of the 19th century, so that they are nearly always recorded in the journals which were already appearing regularly at that time.

My own investigations of a large number of old paintings described in the following pages are concerned with the historical, chemical and technical

[1] *Secreet-Boeck, waer in vele diversche Secrete ende heerlicke Consten | in veelderleye verscheyden materien | uit seker Latijnsche | Fransoysche | Hoochduytsche | ende Nederlantsche Authoren | tesamen en de by een gebracht zijn: Waer van den meestendeel der voorschreven Authoren namen daer by gheciteert worden.* By een vergadert door D. Doctor Carel Batin, Dordrecht, 1609.

(*Secret Book, wherein are collected divers secret and fine arts from certain Latin, French, German and Dutch authors. The names of the greater part of the authors are mentioned therewith.* Collected by Doctor Carel Batin, Dordrecht, 1609.)

data of painting. These data together can form the basis of further investigations concerning the Old Dutch and Flemish Schools. The methods of analysis employed may also be applied to the pigments of other schools of painting in so far as material for investigation which is above suspicion is available, and they can be employed in the study of other fine arts.

All research methods, which can be applied in this province, must satisfy one and the same condition, namely, they must furnish a positive result when only a minimum amount of material for investigation is available.

The painting must not be spoiled in any visible manner in obtaining a suitable specimen. It is thus obvious that for an efficient study only the microscope can lead to a satisfactory result. The microchemical reactions, which are recorded in what follows, can all be carried out with a magnification which need not exceed 100. Since, however, larger magnifications are also always available with a modern microscope, such magnifications can sometimes be an advantage in intensifying the reactions.

In taking the specimens of the paint one must first of all be quite certain that one is dealing with an authentic part of the original painting. It is best to take the specimens from the outer edge of the painting, which is situated in the rabbet of the frame, that is to say, hidden from sight. If this will not do, then one must search for a suitable spot over the visible part. When one considers that a circular specimen of paint, having a diameter of 0·1 mm., furnishes an image with a diameter of 1 cm. under a microscope with a magnification of 100, and

that this size is more than sufficient for these microchemical reactions, then it is clear that there need be no question of any damage to the layers of paint.

In looking for a part of the painting suitable for taking a specimen, one may with advantage make use of a binocular magnifying-glass which is fastened to the head and so leaves both hands free. When one has found a good portion and has first of all convinced oneself of the colour which gives a first identification of the paint, the removal of the specimen may then be effected with a steel needle or the point of a small steel harpoon which has been made sticky with a little Canada balsam. The specimen of paint can now be treated simply as a microscopical preparation, and when there is no opportunity for an immediate examination, it must be provided with an explanatory label and put away. It is, however, recommended that, whenever the opportunity exists, the specimens be examined immediately under the microscope in order to make sure that one is dealing with a specimen of paint, and that one has not, for example, taken a portion of the varnish layer. In view of the dimensions which are sufficient for a satisfactory specimen it is generally difficult, if not impossible, for the person who has taken the specimen, to find again with the naked eye the part from which it was removed.

The actual microscopic examination is the same at first for all kinds of paints. The specimen is first of all stripped of the accompanying Canada balsam. This may be carried out most easily by allowing a drop of xylol, which if possible has been warmed beforehand, to flow several times over it. The Canada balsam thereby is quickly

and thoroughly removed. Further remnants of the varnish layer, such as small amounts of resin, will often accompany the specimen of paint. For this reason washing with alcohol is carried out after the treatment with xylol and the subsequent drying, and the specimen is after that completely free from admixtures. It is desirable to examine it with the microscope after each washing in order to be sure in how far it has been attacked.

The colour may be determined by examining the specimen by reflected light, and one satisfies oneself then whether this colour agrees with that in the original painting. Subsequently one may determine whether one is dealing with a single pigment or with a mixture. For this purpose the specimen is so treated that the grains of the pigment become separately visible. A part of the specimen is put under a drop of water, and to this is added a small drop of dilute alkali with the aid of a platinum wire while the preparation is under observation. The influence of this is immediately noticeable. The edge of the specimen of paint melts away, so to speak, and the separate grains of the pigments thereby become visible. If sufficient grains can be seen, the very dilute alkali is then removed by absorption on a strip of filter-paper, and the preparation is washed several times with water and dried by gentle heating.

For the determination of the colour and the double refraction, if that occurs, it is recommended that the specimen be examined under a liquid, for example, xylol. One then obtains at the same time an idea of the refractive index compared with that of xylol, which is 1·49. The xylol can afterwards be

removed and the preparation treated with other liquids for the determination of the refractive index.[1] The use of cover glasses is not necessary provided that care is taken that the liquids remain spread out flat. These can be removed by absorption on filter-paper and washing, after which the preparation is again dried.

One now usually has the specimen of paint together with a skeleton of dried oil. This latter is generally no hindrance to the proper action of the reagents. Only when relatively new paint is concerned will the action take place slowly, since the oil then acts as a protection. Warming will, however, accelerate it in most cases.

The results of the various investigations are collected together in tables, each dealing separately with a single pigment. In these tables the museums in which the pictures are to be found are indicated by a letter after the names of the painters.

These letters are :

M. for the *Royal Picture Gallery* (*Mauritshuis*) at the Hague, Holland.

R. for the *Rijks Museum* at Amsterdam, Holland.

G. for the *Municipal Museum* (*Gemeente Museum*) at the Hague, Holland.

F.H. for the *Frans Hals Museum* at Haarlem, Holland.

Midd. for the *Municipal Museum* (*Raadhuis*) at Middelburg, Holland.

A. for the *Royal Museum of Fine Arts* at Antwerp, Belgium.

[1] In this connection see Kley, *Mikrochemische Analyse*, Leipzig, 1921, part i. p. 268.

The numbers recorded after these letters correspond to those of the 1927 catalogue of the museums concerned; after these follow the English titles of the paintings as far as these are available.

The pictures investigated are arranged in the tables in chronological order independently of the museum in which they are to be found. The dates correspond to those which occur on the pictures unless they are known with certainty in some other way. Wherever only the approximate date can be recorded an asterisk (*) is placed above the year.

If the same picture occurs twice in the table of one pigment, then this refers to two specimens taken from different parts of the painting.

Finally, all the specimens of paint analysed and the main facts concerning them are displayed in a graphical representation from which a clear picture may be obtained of the periods during which the various pigments were used.

The microphotographs were prepared with the aid of optical apparatus supplied by the firm of Zeiss.

All reproductions were prepared from my own photographs, unless the contrary is stated.

In working out the microchemical reactions commercial oil paints supplied by the firms Winsor & Newton of London and Talens of Apeldoorn, Holland, were used.

In addition the collection of specimens of pigments dating from the beginning of the 19th century which was formerly the property of the firm of Hafkenscheid of Amsterdam, Holland, and is now in the possession of the Inorganic Chemical Laboratory of the Technical University of Delft, Holland, has been of great assistance.

CHAPTER II

BLUE PIGMENTS

¶ Natural Ultramarine

Even the oldest writings on the technique of painting[1] make mention of this very beautifully coloured pigment, the pure blue of which has not up to the present day been equalled by any synthetic product. It forms the coloured constituent of lapis lazuli (lazurite) and is often known by this name, frequently also as "lapis" for short.

By a lengthy "mud" process the coloured part can be separated from the large quantity of colourless admixtures, of which calcspar is the most important. There are several descriptions of this "mud" process in the manuscript by Mayerne,[2] which though differing in detail agree on the main points. The pieces of mineral are first heated, and then by sudden cooling in water are reduced somewhat in size. After being further finely powdered, they are treated with vinegar in order to remove a large part of the colourless calcspar. Sometimes these two treatments are combined and the heated mineral is cooled in vine-

[1] Theophrastus, *De Lapidibus*, already mentions the use of lapis lazuli as a pigment, probably, however, only the powdered mineral without any preliminary purification.

Pliny, *Historia Naturalis*, Books xxxvii., xxxviii., mentions the occurrence of gold vanes (pyrites) in the "cyanus."

[2] Sir Theodore Turquet de Mayerne collected a large number of the technical data of painting in a manuscript, the beginning of which dates from 1620 and which is to be found in the British Museum in London. It has been translated and edited by Ernst Berger and was published in his *Beiträge zur Entwicklungsgeschichte der Maltechnik*, Munich, 1901, part iv.

gar. The powder is subsequently taken up in a paste which is composed of some kind of resin (mastic or colophony), bees' wax, linseed oil and turpentine. The plastic mass thus obtained is kneaded under water, in which a little alkali carbonate is dissolved. As a result the blue constituent passes into the water phase, and the impurities, among which there is always a little pyrites, remain behind in the mass of paste. By successively kneading with fresh quantities of water we obtain a blue product of decreasing quality and colour; the product which is obtained by the last kneadings is known as "ultramarine ash" and consists almost exclusively of calcspar together with a few blue particles, and has a light grey-blue tint.

A similar purifying process has been very completely described by Bouvier,[1] who used it to purify the mineral for his own use.

The process is probably the oldest form of the so-called "flotation process". Dr. Scott Taylor informed me that the pigment is still always obtained from the mineral in such a way by Messrs. Winsor & Newton of London.

It is clear that the purification of the mineral is a lengthy process and this, together with the rare occurrence of lapis lazuli, makes the "diamond of the pigments"[2] a valuable possession. Even the *Secret Book* mentions this and calls ultramarine "of all blues the most costly, since it is but seldom to be found". Another later illustration of this is the estimated value of "a box with various kinds of ultramarine, worth 10 to 60 guilders per ounce", from the

[1] *Manuel des jeunes artistes et amateurs en peinture*, Paris, 1827.
[2] Mayerne manuscript, p. 76, verso.

bequest of Cornelis Dusart (1660–1704). There is also the well-known declaration of Walpole [1] in his story of Anne Carlisle. "She was in such favour with King Charles that he presented her and Vandyck with as much ultramarine at one time as cost him above £500".

The recipes for the purification of the mineral are of Italian origin, and it is very probable that the "mud" process was principally carried out in Italy, and the pure natural ultramarine despatched from there as a commercial product. It is also possible that quantities of the purified mineral were obtained directly from India; a letter from Cornelis Claesz Heda from India,[2] dated March 23, 1617, at least gives an indication of this.

The high price of natural ultramarine has always stood in the way of its general use, and this is still the case, though the demand has also become smaller on account of the larger number of blue pigments available.

With regard to the chemical constitution of natural ultramarine it is obvious that the analyses of it, which have been made and which refer to a product of very varying degrees of purity, can hardly agree among themselves. A result of this disagreement is that even the question whether or not natural ultramarine can really be taken to be a definite compound remains unconsidered.

The lapis lazuli, which is found in various parts of Eastern Asia, in Persia and also in South America, has not always the same appearance; the colour

[1] *Anecdotes on Painting*, London, 1786, p. 197.

[2] A. van der Willigen, Pz., *Les artistes de Haarlem*, The Hague, 1870.

varies from dark blue, sometimes with a somewhat violet shade, to light blue.

Further, from the very nature of the process of purification, such a treatment can bring about no absolute separation from the surrounding calcspar.

Various analyses have been carried out even at the beginning of last century, and all have been collected in an admirable bibliography by Hoffman.[1] The most important analyses are those of Désormes and Clément.[2] They purified the mineral according to the old kneading process and obtained a yield of 2 to 3 per cent. The method is described by them as a "savonnage". The percentage composition of the purified product was then given.[3] Further analyses were then carried out by Brögger and Backström,[4] who took as the starting-point a piece of lapis lazuli of selected quality which contained as little calcspar as possible. This was purified in an extremely accurate manner, by which they obtained a yield of 0·42 per cent, which was then analysed. This latter product was free from calcspar, as was shown by the analysis.

The recent investigations of Jaeger, Westenbrink and van Melle[5] have shown unequivocally that in the case of natural ultramarine and of the closely related synthetic ultramarine as well, there is no question of

[1] *Das Ultramarin*, Braunschweig, 1902.

[2] *Annales de chimie*, 1806, p. 317, *Mémoire sur l'outremer.*

[3]

Silice	35·80 per cent.
Alumine	34·80 „
Soude	23·10 „
Soufre	3·10 „
Carb. de chaux	3·20 „

[4] *Zeitschrift für Krystallographie*, 1891, part xviii. p. 209.

[5] *Proceedings of the Royal Academy of Sciences at Amsterdam*, 1927, part xxx. pp. 249-267, 479-498, 885-904.

a constant compound or a simple stoichiometric relation, so that a rational formula cannot be given. It is consequently simplest to conceive natural ultramarine as a sodium aluminium silicate in which sulphur occurs in variable amounts as sulphide. The colouring power would then also have to be ascribed to the presence of sulphur.

Natural ultramarine ground to a paint with oil lends itself chiefly to being spread in a thin coloured layer which is transparent to a certain extent, and hence brings out the effect of the underlying painting. This mode of application is called "glazing" and was already used to a considerable extent by the primitive painters; one may even say that their whole technique was based on this method of painting.

Natural ultramarine must be reckoned as one of the few pigments whose appearance is liable to change in time. Although by far the greater number of the pictures in which this pigment is used are still to be seen in their original state, there are cases in which the paint loses its beautiful blue colour and takes on a greyish-blue tint, which gives the picture a strange appearance. The phenomenon is known under the name of "ultramarine sickness", the cause of which remained unknown for a long time and is perhaps not yet completely elucidated.

G. van der Sleen[1] believed that the cause must be sought in the presence of sulphur dioxide in the atmosphere, and has experimentally produced "ultramarine sickness", or at least a very similar phenomenon, by the action of this gas. He put drops of water on a layer of natural ultramarine paint a few

[1] *Archives du Musée Teyler*, 1922, série iii. vol. v., *Quelques recherches à propos du nettoyage des tableaux de Frans Hals à Harlem*, p. 36.

weeks old spread on glass, and then allowed the whole to remain some time in an atmosphere of sulphur dioxide. Afterwards the paint was brought into the air again, and after a few hours cracks and a discoloration of the pigment were visible in the places where he had put the drops of water. According to this explanation the sulphurous acid, which is present in the drops of water, becomes oxidised to sulphuric acid by the peroxides of the dried oil. As the water evaporates into the air the concentration of the sulphuric acid becomes so strong that it has a decomposing action on the natural ultramarine, which thereby acquires a whitish appearance.

If the cause must be sought along these lines, then in any case the attacking action is very much exaggerated in these experiments and the reaction much accelerated. That the presence of water on the surface of the paint is an essential point has been confirmed by my own experiments. A layer of ultramarine (ground with linseed oil) spread on glass and about two years old was afterwards kept for half a year in a desiccator in which were a little sodium sulphide and some concentrated sulphuric acid in order to obtain an atmosphere of dry sulphur dioxide. At the end of this time some bleaching was indeed observable, but this was in nowise visible over the whole layer of paint. Afterwards a few drops of water were also put on the layer of paint and these, even after a 24 hours' stay in the desiccator, showed their influence by completely discoloured patches.

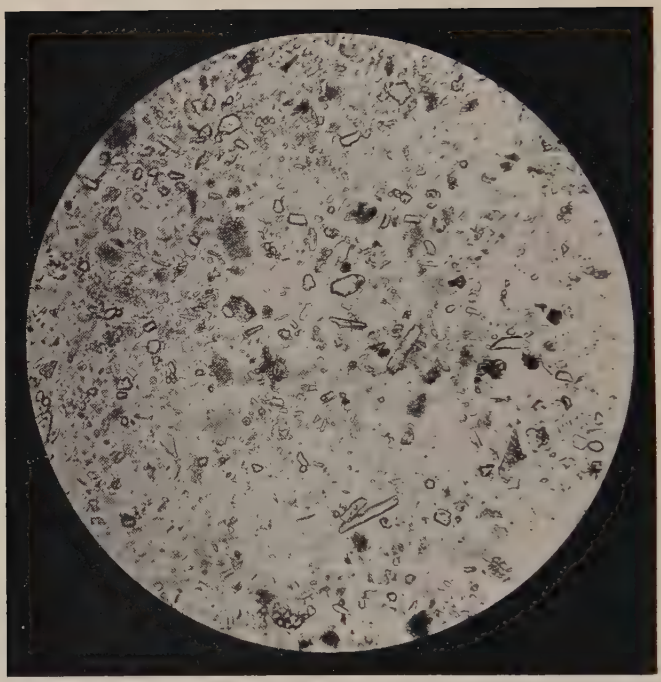
From a microscopical examination of two known cases of "ultramarine sickness", viz.:

Jan Steen. (M. 170.) *The Brewery of Jan Steen*
Gerard Dou. (M. 32.) *The Young Mother*

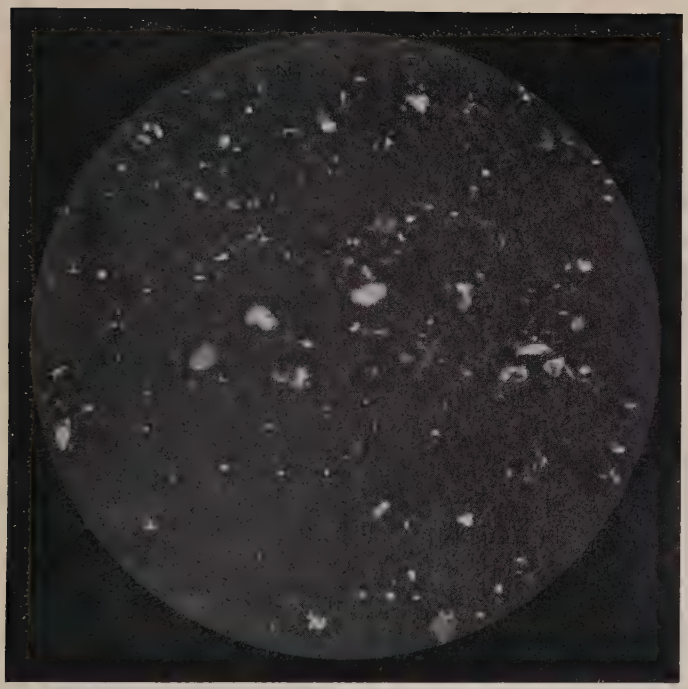
it appeared that there was no question of a uniform action of a gas on the whole surface of the painting; blue particles are still clearly to be seen in the "sick" parts without exception, while the decolorised parts are to be found mainly at the edges of the cracks. This latter fact shows that the "sickness" has occurred after the formation of the ordinary crackle, hence at a time when there were no longer any peroxides present in the dried oil of the paint-layer. Further, it appeared at the same time that the phenomenon is delayed or hindered by certain underpaintings, a circumstance which shows that there were other causes at work. One of these may be that the acid which is responsible for the decolorising action was present either in an underpainting or in a later glazing or varnish, or was produced therein, which may be the reason why the decolorising action makes itself most felt at the edges of the cracks.

In any case it may be taken as established that "ultramarine sickness" is a decomposition of the original pigment which cannot be made to proceed in the opposite direction; that is to say, the blue colour cannot be restored.

When examined under the microscope (Plate 1) natural ultramarine shows a number of clear blue transparent particles which have the appearance of a crumbled mineral and are of very varying size. Between these there are to be found, without exception, colourless particles of calcspar, the residues of the surrounding stone which are clearly visible, especially between crossed nicols (Plate 2). It is particularly characteristic that the blue particles are not birefringent; the colourless particles of calcspar are



1. NATURAL ULTRAMARINE (105×)



2. NATURAL ULTRAMARINE (105×)

The same specimen between crossed nicols

present to a less extent in proportion as the quality of the ultramarine is better, but they are never absent.

After natural ultramarine has already been identified with practical certainty by these optical properties, the detection of sulphur in the pigment is the only characteristic reaction necessary.

The specimen of paint, which for this purpose is placed in the bottom of a hollow-ground microscopical slide, is treated with dilute acetic acid, whereby the accompanying calcspar is dissolved, but the blue particles remain unaltered.[1] After washing and drying a very small drop of dilute hydrochloric acid is added, and at the same time the hollow in the slide is covered with a cover-glass, which is provided on its under side with a small piece of thin filter-paper moistened with a little lead acetate solution. The trace of hydrogen sulphide obtained by the action of the hydrochloric acid on the mineral immediately acts on the lead acetate and gives a brown stain of lead sulphide on the filter-paper, which is usually visible even to the unaided eye.

The reaction is very sensitive, but care should especially be taken that the amount of hydrochloric acid is small, since otherwise there is a chance that the hydrogen sulphide will remain dissolved in it.

There is a chance of failure when the natural ultramarine is mixed with white lead. In this case the specimen of paint is treated directly with hydro-

[1] The statement of Laurie that acetic acid may have a decomposing action upon natural ultramarine could not be confirmed. Indeed, as appears from the old recipes, warm acetic acid is actually used in the purification of the mineral. See *The Pigments and Mediums of the Old Masters*, 1914, pp. 40, 55.

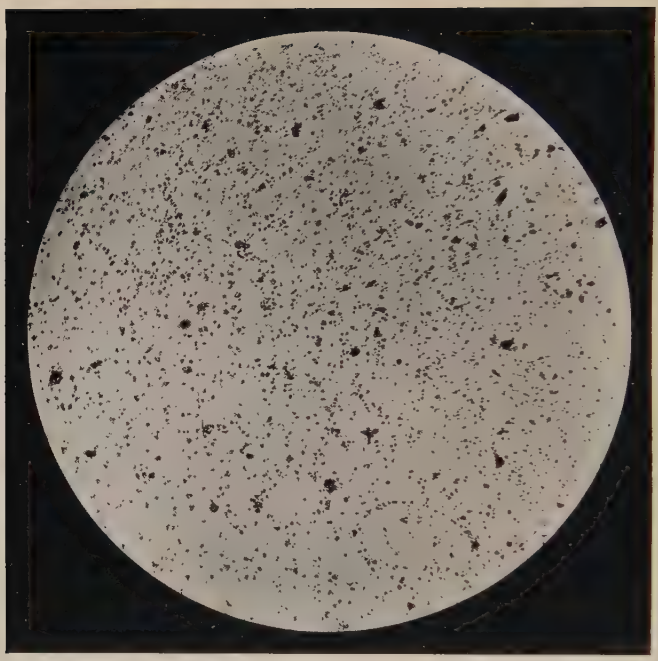
chloric acid and is at the same time observed with a microscope by reflected light. Around the blue particles there soon appears a brown coloration of the white lead through the formation of lead sulphide which is very clearly noticeable.

In both ways of acting on the hydrogen sulphide there is an opportunity of following the discoloration of the blue particles by the hydrochloric acid often from the edge of the specimen of paint to the centre.

The following list of 16 *specimens of natural ultramarine clearly indicates that this pigment has been used throughout the ages.*

In the investigation it was also shown that besides blue particles, colourless ones of calcspar were present in all cases to a greater or lesser extent.

1437. Jan van Eyck. (A. 410.) *Saint Barbara.*
1450. *Rogier van der Weyden. (A. 393.) *The Bloodless Offering of the New Covenant, Symbol of the Bloody Offering of Golgotha.*
1500. *Quinten Metsijs. (A. 29.) *Saint Christopher.*
1509. Quinten Metsijs. (A. 245.) *St. John the Baptist beheaded.*
1590. *Ambrosius Francken, the Elder. (A. 573.) *Christ in the Tomb.*
1600. *Wyttewaal. (M. 223.) *Mars and Venus.*
1600. *Pieter Breughel, the Elder. (Copy, A. 776.) *The Census at Bethlehem.*
1601. Marten de Vos. (A. 83.) *The Tribute to Caesar.*
1630. *Van Dyck. (A. 407.) *Portrait of a Little Girl.*
1650. *Quinten Metsijs. (Copy, A. 565.) *The Virgin embracing the dead Christ.*
1660. *Vertangen. (G.) *Arcadian Landscape.*
1665. Hanneman. (G.) *Portrait of Elisabeth van Limborgh.*
1671. Vaillant. (R. 2341.) *Portrait of Maria van Oosterwyck.*
1710. *Van Huysum. (M. 71.) *Flowerpiece.*
1750. *Ten Compe. (G.) *The Plein at the Hague.*
1810. *J. F. Valois. (G.) *The Mauritshuis at the Hague.*



3. SYNTHETIC ULTRAMARINE (105×)

¶ Synthetic Ultramarine

As early as 1814 it was noticed by Tassaert that the formation of a blue substance had taken place in various ovens where the Leblanc soda process was carried out. He put this substance at the disposal of Vauquelin, who analysed it and showed its connection with natural ultramarine. The demand which then existed for a cheap and at the same time reliable blue pigment led the Société d'Encouragement pour l'Industrie Nationale to offer a prize in 1824.

The prize was awarded in 1828 to Guimet of Toulouse, who did not publish his process, but as early as 1831 set up a factory for the preparation of the synthetic ultramarine which he had discovered. At the same time the same discovery was made quite independently of Guimet by Gmelin of Tübingen.[1] As might be expected an extensive polemic as to the priority of the discovery was carried on in the French and German literature of the subject; it is, however, certain that various factories were erected in the two countries relatively shortly after the discovery.

Synthetic ultramarine is to-day one of the cheapest blue pigments. The preparation consists mainly of the long-continued heating of the mixed powders of kaolin, infusorial earth, sodium sulphate, soda, sulphur and wood-charcoal or resin in definite proportions. By changing these, products can be obtained with various shades from light green to light red or violet. The blue product is, however, by far the most important.

[1] *Annales de chimie et de physique*, 1828, tome 37, p. 414; *Annalen der Chemie und Physik*, 1828, part xiv. p. 363.

Although from a chemical point of view it is very closely related to natural ultramarine, one never meets in synthetic ultramarine with the pure blue colour of the natural. Generally one may perceive a kind of purple tinge in the synthetic product which gives the blue colour a "hard" appearance. This difference is very conspicuous, particularly in artificial light.

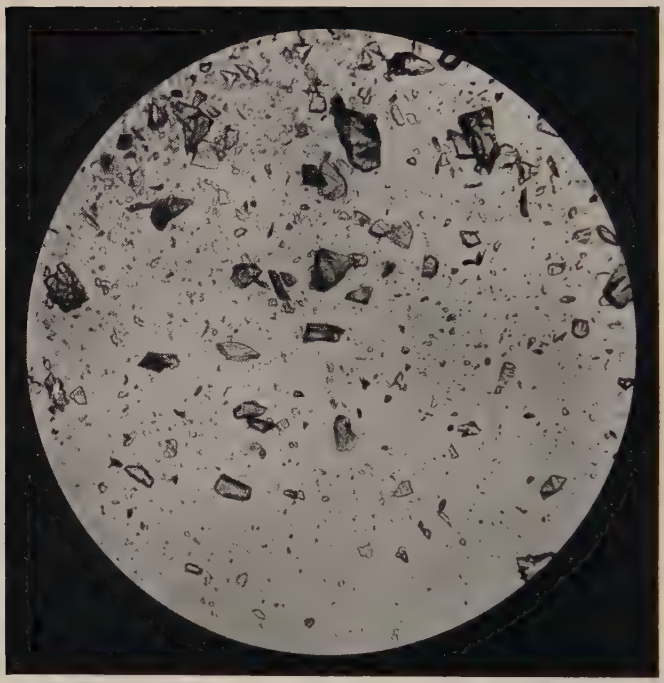
When examined under the microscope (Plate 3), synthetic ultramarine also shows a noticeable difference from the natural product. The particles of pigment have all more or less the form of spheres and show but little variation in size. They are much less transparent than the particles of natural ultramarine, so that the determination of a refractive index cannot be made with certainty. No traces of birefringent impurities can be seen between crossed nicols; the product is completely homogeneous and extremely finely divided.

Consequently this pigment can be identified with certainty, even from its external appearance. The presence of sulphur is also characteristic of it, and this can be detected in the same way as with natural ultramarine. Since no impurities are present, no preliminary treatment with acetic acid is necessary.

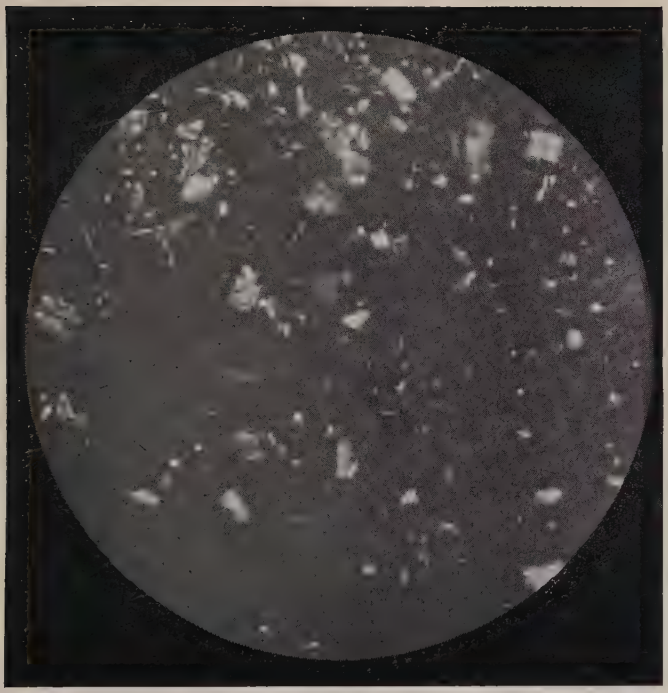
It is noteworthy that in this case the pigment is very quickly discoloured even by acetic acid, in contrast with the natural product.[1]

No synthetic ultramarine was encountered in the specimens of blue pigment which were investigated.

[1] Also observed by Gentele, *Lehrbuch der Farbenfabrikation*, Braunschweig, 1906, part i. p. 51.



4. AZURITE (105×)



5. AZURITE (105×)

The same specimen between crossed nicols

¶ Azurite

This mineral, a basic copper carbonate of the composition $2CuCO_3.Cu(OH)_2$, is found in various places in Europe, generally together with the nearly related mineral, malachite. It does occur in a well crystallised form and is then very pure, but it is usually accompanied by impurities. The product prepared as a pigment may therefore have a different appearance according to the degree of purity, as a result of which it was formerly known under various names. In the *Secret Book*[1] mention is made of "Ash Blue" (Asch-blau), but this is clearly confused with the then still little-known smalt. Goeree[2] speaks of "Blue Ash" (Blaauwe-Asch) or "Sky Blue" (Hemels-Blaauw), which "is found in various sorts, high and low in colour" (word van verscheide soorten, hoog en leeg van koleur gevonden). The names "Mountain Blue" (Bergblauw) and "German Ash" (Duitsche Asch) also occur.

Examined under the microscope (Plate 4), the form of azurite shows a strong resemblance to that of glass powder; the particles are very irregular in size and frequently have the appearance of splinters. In addition green-coloured particles of malachite are almost without exception to be found beside the blue particles of azurite. All the particles are strongly birefringent (Plate 5) and possess a refractive index above that of methylene iodide ($n = 1{\cdot}74$).

When the specimen of azurite is treated with dilute nitric acid, solution takes place directly with effer-

[1] P. 221.

[2] *Verligterie-Kunde*, Amsterdam, 1697, p. 16.

vescence. After it has been evaporated to dryness and taken up in dilute acetic acid a trace of lead acetate is added and an excess of potassium nitrite. The presence of copper is confirmed by the formation of a triple nitrite of copper, potassium and lead, $K_2CuPb(NO_3)_6$ —the so-called triple nitrite reaction (Plate 6). Since a trace of lead will practically always be present in the specimen of paint, the addition of the lead acetate can generally be omitted. At the time of the primitive painters azurite was the only blue pigment which was used besides ultramarine; the two pigments have indeed been confused with one another. An example of this is the attempt of Mayerne to purify azurite by the method which is employed for lapis lazuli and entirely failed.[1] In their external appearance the two pigments, especially when in the dry state, are very similar. When ground in oil natural ultramarine is a much purer blue, while azurite has a much "harder" tint, sometimes with a somewhat greenish tinge. The latter may, however, be caused by a small amount of malachite, which is encountered in nearly all the specimens investigated.

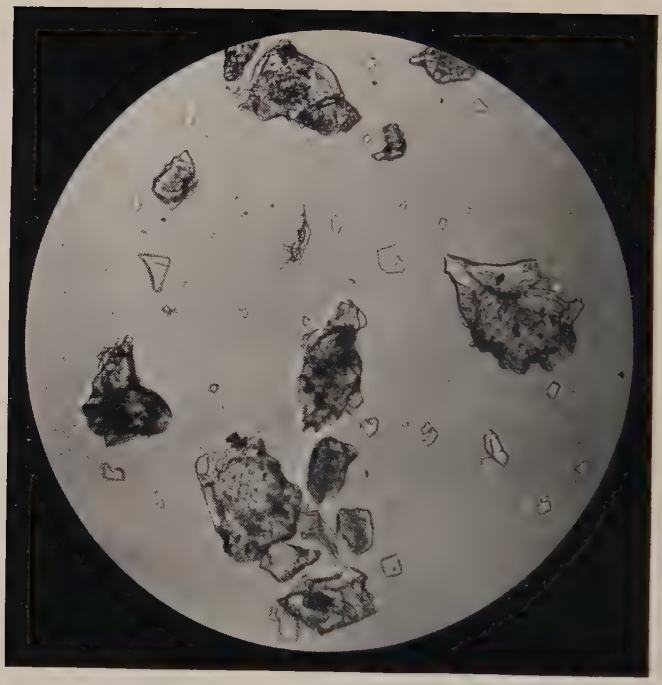
On account of the great similarity in the shape of the particles, the colour, and the equal possession of the property of double refraction, azurite can very easily be confused with the so-called Egyptian blue, the use of which as a pigment is not inconceivable. A detailed investigation into the nature of this substance was made by Laurie, McLintock and Miles,[2] who obtained a product completely identical with the blue occurring on ancient Egyptian paintings.

[1] P. 15, verso.

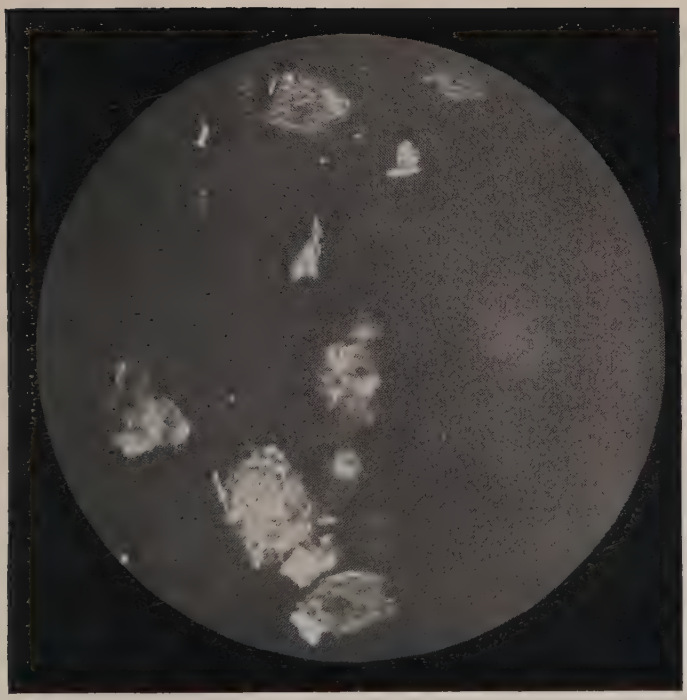
[2] *Proceedings of the Royal Society of London*, A., vol. lxxxix. p. 418.

6. POTASSIUM-COPPER-LEAD NITRITE (210×)

Triple nitrite reaction



7. EGYPTIAN BLUE (105×)
Museum of Antiquities, Leiden



8. EGYPTIAN BLUE (105×)

The same specimen between crossed nicols

They heated together fine sand, calcium carbonate, copper carbonate and a flux (nature not given), and thereby obtained a compound $CaO.CuO.4SiO_2$, of which, among other things, they determined the refractive index, which was 1·63. The same refractive index was observed with the specimen of Egyptian blue, kindly given to me by the director of the Museum of Antiquities at Leiden, Holland (Plates 7 and 8), here reproduced, and this refractive index therefore lies below that of azurite. A ready distinction is also to be found in the chemical reaction; Egyptian blue is not dissolved by nitric acid. For its further identification the reader is referred to the treatment of smalt here below.

The following list of 19 *specimens of azurite investigated show that this pigment was in general use during the* 16*th and* 17*th centuries, which is a confirmation of the period determined by Laurie from literary data.*[1]

1490. *Hans Memling. (A. 780.) *Angels playing various instruments.*
1500. *Hieronymus Bosch. (A. 840.) *Our Saviour mocked by the Soldiers.*
1510. *Antwerp Master. (A. 385.) *Jesus in the midst of the Scribes.*
1515. Jakob Cornelisz van Oostzanen. (A. 525.) *The Donor's Wife.*
1525. Barend van Orley. (A. 741.) *The Last Judgement and the Seventh Work.*
1530. *Jan Swart. (A. 207.) *The Adoration of the Kings.*
1530. *Bruges Master. (A. 535.) *The Holy Virgin.*
1540. *School Engebrechtsz. (A. 532.) *Before the Crucifixion.*
1570. *Master of the South-Netherlands. (A. 548.) *Mater Dolorosa.*
1600. *Jan van Eyck. (Copy, A. 415.) *The Holy Pilgrims.*

[1] *The Pigments and Mediums of the Old Masters*, 1914, p. 136.

1610. *Pieter Breughel, the Younger. (A. 644.) *Flemish Fair.*
1610. *Pieter Breughel, the Elder. (A. 926.) *Landscape.*
1615. *Rubens. (A. 319.) *Christ wept over by Saint John and the Holy Women.*
1615. *Rubens. (A. 312.) *Our Lady with the Parrot.*
1620. *Jacob Jordaens. (A. 844.) *Meleager and Atalanta.*
1635. Van Dyck. (A. 404.) *Christ in the Grave.*
1640. *Lapp. (M. 84.) *Italian Landscape.*
1658. Bega. (M. 400.) *Tavern Scene.*
1660. *Van der Helst. (M. 545.) *Portrait of a Young Lady.*

¶ Smalt

From the period in which objects were first made in glass also dates the art of producing these objects in blue-coloured glass. The analysis of a number of specimens of ancient Egyptian glass by Neumann[1] showed that at this period copper was used exclusively for the production of a blue colour. According to the same investigator cobalt was first used in Venice in 1443 for colouring glass blue. By the addition of small quantities of roasted cobaltite (CoAsS) or smaltite ($CoAs_2$) a mass of glass is turned blue through the formation of cobalt-silicate. The process, however, appears to have been carefully kept secret for a long time—at least the first commercial production of cobalt glass, with the object of employing it in a finely powdered state as a pigment, was carried out at about the middle of the 16th century by Schürer in Saxony.[2]

Originally the product was only used in the manufacture of pottery for making blue glazes, but

[1] *Zeitschrift für angewandte Chemie*, 1925, vol. xxxviii. pp. 776 and 857; 1927, vol. xl. p. 963; 1928, vol. xli. p. 203.

[2] Guignet, *Fabrication des couleurs*, Paris, 1888, p. 87.

even at the beginning of the 17th century it came into general use as an oil-paint.

In the finely powdered state smalt has but little colour, and in order that it may serve as a pigment it is necessary to employ the product in a relatively coarse form, so that it is, for example, less suitable for the portraying of fine details.

The paint substance which one obtains from smalt and oil is very difficult to spread. The smalt always has a tendency to settle out in the mass of paint, and if one wants to keep the mass so thin that it can be spread out, the smalt tends to trickle down the vertical surface of the picture. This great drawback can be overcome by adding a little white lead to the smalt, but by this means the already not very intense colour is necessarily made lighter.

Karel van Mander[1] in the 17th century had already stated how one could overcome this drawback occurring when smalt was used unmixed. One applied the smalt to a roughened surface, whereby a better adhesion occurs; also the painting was covered with blotting-paper, which absorbed part of the oil from the paint; the paint then became more viscous and no longer trickled down the surface of the picture.

Another method appears to have been employed by Rubens;[2] he mixed the smalt with a volatile oil which probably contained in addition a little resin. When it is spread out the oil evaporates relatively quickly, and the smalt now remains behind, held by the resin.

[1] *Het Schilder-Boeck*, Haarlem, 1604, end of the 12th chapter.

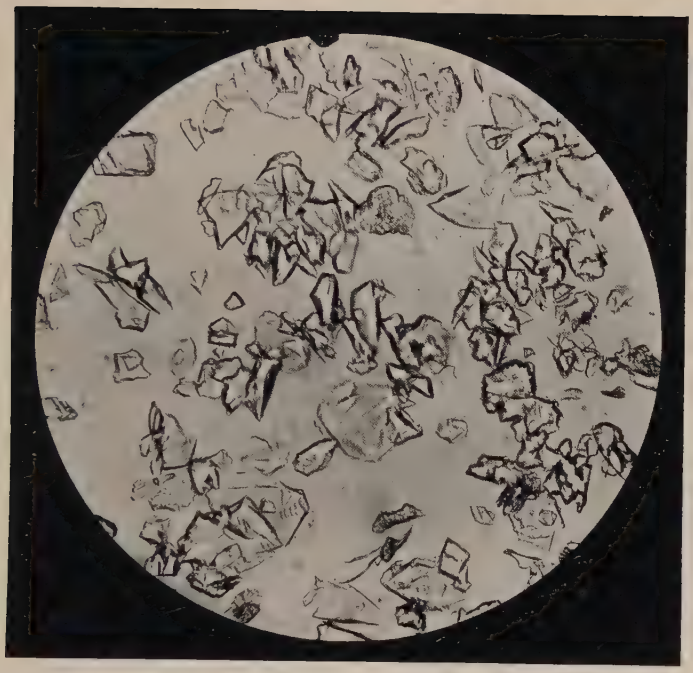
[2] Eastlake, *Materials for a History of Oil-painting*, 1847, chap. xiii.

Paintings carried out with unmixed smalt are always characterised by a peculiar granular appearance, a consequence of the coarse nature of the pigment.

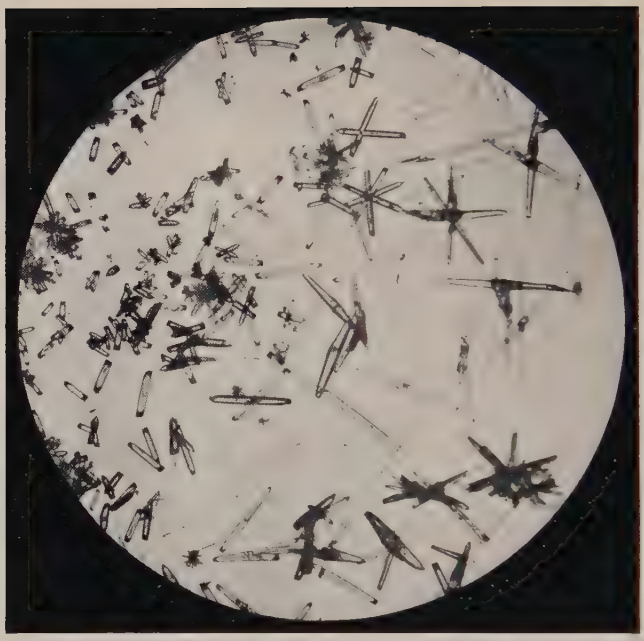
Even with low magnifications the appearance of smalt under the microscope reflects the true glassy character of the substance (Plate 9), that is to say, splinters and angular pieces are visible. By transmitted light it can be clearly observed that the colour is not very intense by comparison with other blue pigments. There is no double refraction, and a determination of the refractive index shows that it lies below that of nitro-benzene ($n = 1{\cdot}55$). For the determination of the refractive index the smalt may readily be separated from the white lead which nearly always surrounds it, by dissolving the latter in nitric acid, then washing and drying.

Smalt is attacked in time by strong hydrochloric acid or *aqua regia*, but this method of solution is not certain enough to detect the characteristic constituent cobalt when only small quantities are available. For this purpose the specimen of paint is, without any preliminary treatment, ignited on a platinum spatula with excess of concentrated sulphuric acid, whilst in addition a few grains of iron-free ammonium fluoride are added. The nascent hydrogen fluoride attacks the glass, and the cobalt present is converted into cobalt sulphate by the excess of sulphuric acid. It is best to repeat the ignition with concentrated sulphuric acid, and particularly not to heat to redness, since otherwise there is a danger of the formation of cobalt oxide, which will not dissolve during the taking up in acetic acid which follows.

The lead sulphate which may be present settles



9. SMALT (105×)



10. COBALTOUS-MERCURIC-THIOCYANATE (105×)

11. COPPER-MERCURIC-THIOCYANATE (105×)

and has no influence on the further course of the reaction. The clear solution, which one can decant if necessary, now contains cobalt sulphate and is confirmed after adding ammonium-mercuric-thiocyanate, when the characteristic intensely blue coloured crystals of the corresponding cobalt compound are formed (Plate 10). Generally one will, however, only find the smallest forms of these crystals, since the original amount of cobalt is always very small and only forms a small percentage of the quantity of smalt available.

If larger amounts of smalt are to hand, the well-known reaction with the borax bead can also be carried out successfully, but then preferably by forming the bead on the end of a thin straight piece of platinum wire.

The test for the Egyptian blue, mentioned in the section on azurite, can be carried out in a similar manner. The characteristic copper can be detected in the residue on the spatula either with ammonium-mercuric-thiocyanate (Plate 11) or with the triple nitrite reaction (Plate 6).

The 16 specimens of smalt investigated date from the 16th and 17th centuries, as appears from the following list.

No specimen of Egyptian blue was encountered.

1620. *Rubens. (Copy, A. 315.) *The Descent from the Cross.*
1630. *Salomon van Ruysdael. (M. 566.) *Landscape.*
1640. *Van Goyen. (M. 674.) *A Riverside Town.*
1644. Van der Laeck. (G.) *The Nieuwburg Mansion.*
1647. Ant. Palamedesz. (R. 1837 a.) *A Guardroom with Soldiers.*
1650. *Verbeecq. (M. 611.) *Two Horsemen near a Brook.*
1650. *Jan Steen. (G.) *The Riviervischmarkt at the Hague.*
1650. *Lingelbach. (M. 87.) *The Hay-harvest.*
1663. Van der Croos. (G.) *A View of the Hague.*

1663. Van der Croos. (G.) *A View of the Hague.*
1670. *Willem van de Velde. (M. 471.) *The Surrender of the English Flag-ship "Royal Prince".*
1693. Ludolf Bakhuysen. (M. 7.) *A Dutch Harbour.*
1702. Ludolf Bakhuysen. (R. 409 f.) *The Families Bakhuysen and de Hooghe.*
1707. Ludolf Bakhuysen. (R. 418.) *A Painter in his Studio at work on a Lady's Portrait.*
1750. *Ten Compe. (G.) *The Plein at the Hague.*
1780. *Storck. (M. 174.) *Beach-scene.*

¶ Cobalt Blue

Smalt disappeared from the painter's palette more than a century ago, and has been replaced by cobalt blue. The honour of discovering this pigment belongs to Thénard, who in 1802 was looking for a blue pigment which might replace the expensive natural ultramarine and the often less stable Prussian blue.[1] He was guided in his investigations by certain data which were available from the porcelain works at Sèvres, where it was known how to obtain a blue porcelain by means of cobalt oxide.[2] He succeeded, by adding together cobalt phosphate and aluminium hydroxide and then drying and igniting the mixture, in producing an excellent blue pigment which is still named after its discoverer. Since the new pigment satisfied a recognised demand it was employed everywhere relatively soon after its discovery,[3] especially in France, as was natural.

[1] *Journal des Mines*, 1802, part lxxxvi. p. 128, *Considérations générales sur les couleurs, suivies d'un procédé pour préparer une couleur aussi belle que l'outremer.*

[2] Guignet et Garnier, *La céramique ancienne et moderne*, Paris, 1899.

[3] Laurie incorrectly gives the date of the discovery as 1820–1830, *The Pigments and Mediums of the Old Masters*, 1914, p. 16.

The varieties of cobalt blue now manufactured are prepared in an analogous manner, though the cobalt can be added in a variety of forms, by which various shades can be obtained.

The addition of cobalt as carried out by Thénard, namely, as phosphate or arsenate, is in a most remarkable manner exactly suitable for the production of a very fine blue colour, as has been shown many years later by Vanino.[1] In a specimen of cobalt blue from the Hafkenscheid collection, in which it occurs under the name of "véritable bleu de Thénard" (Plate 12), phosphoric acid could actually be detected by means of ammonium molybdate. This, however, did not appear to be possible with certain specimens of recent date. Hedvall's extensive investigations[2] have shown the existence of the blue compound, $CoO.Al_2O_3$; there is, however, always an excess of Al_2O_3 present in the pigment. A green compound, $7CoO.5Al_2O_3$, was also found by Hedvall.

When examined microscopically (Plate 13) cobalt blue appears to be a homogeneous product, consisting almost exclusively of rounded grains, not all of the same size but on the whole of very small dimensions. The difference from smalt is therefore extraordinarily clear. The refractive index of cobalt blue lies above that of nitrobenzene, while that of smalt lies below it. No birefringence can be observed.

Obviously the detection of cobalt is the most important point in connection with this pigment. For this purpose the specimen of paint is, without any previous treatment, ignited several times on a platinum spatula with concentrated sulphuric acid.

[1] *Chemiker Zeitung*, 1911, part xxxv. p. 497.
[2] *Zeitschrift für anorganische Chemie*, 1915, part xcii. p. 301.

As with smalt, it is then taken up in acetic acid and the cobalt confirmed as cobaltous-mercuric-thiocyanate (Plate 10).

When larger quantities are available cobalt can also be confirmed by means of the borax-bead test.

The great stability of the colour of cobalt blue and its being unaffected by atmospheric influences make this pigment very suitable for all purposes.

Only the 2 specimens mentioned below appeared to contain cobalt blue, hence it follows that its use did not penetrate into Holland directly after the discovery.

1840. *B. J. VAN HOVEN. (G.) *The Heerengracht at the Hague.*
1860. *L. J. KLEYN. (G.) *A View of the Hague.*

¶ Indigo

This organic colouring matter was an important article brought from the East Indies in the 17th century. By far the greater quantity was, however, used for dyeing fabrics, and only a little was employed as an oil-paint.[1]

When it is mixed with oil the colouring matter becomes very finely divided in the oil, so that no separate grains are microscopically visible, and one generally gets the impression that the colouring matter has dissolved in it. Under higher magnifications (1500 ×) one can, however, clearly see fine particles which possess an intense blue colour.

On account of this intimate envelopment by oil it is not possible to reduce the indigo to indigo white. Since, however, the appearance under the microscope is so extraordinarily characteristic, one can be

[1] Thorpe, *Vat Colours*, 1923, gives a clear description of the way in which the dyeing was previously carried out.

satisfied with proving the organic character of the substance, which can most simply be carried out by bleaching the colouring matter with an alkaline solution of chlorine, this reaction being easily followed.

It is remarkable, considering the small number of blue pigments available in the 17th century, that indigo was used so seldom. According to Church[1] this is to be ascribed to the fact that the indigo then available was not sufficiently pure to be used satisfactorily as an oil-paint. Mayerne[2] has also pointed this out, and recommends that the indigo be treated beforehand with acetic acid.

When prepared as an oil-paint, indigo has a place of its own; it can to a certain extent be used as a covering-paint, but it can be worked up specially well as a glazing-paint. The colour cannot be compared with that of any of the other blue pigments; it approximates most nearly to that of Prussian blue.

The 4 specimens of indigo mentioned below show how little this pigment was used in earlier times considering the total number of specimens of blue pigment which have been analysed.

1610. *Hendrik Pot. (M. 475.) *A Merry Party.*
1627. Frans Hals. (F.H. 125.) *Banquet of Officers of the Civic Guard of St. Adrian.*
1633. Frans Hals. (F.H. 126.) *Assembly of Officers of the Civic Guard of St. Adrian.*
1639. Frans Hals. (F.H. 127.) *Officers and Subalterns of the Civic Guard of St. George.*

[1] *The Chemistry of Paints and Painting*, 1915, p. 243.
[2] P. 144, verso.

¶ Prussian Blue

This pigment was discovered in Berlin by Diesbach[1] at the beginning of the 18th century, probably as early as 1704. He succeeded in keeping his process a secret for about twenty years and in carrying it out in collaboration with Dippel.

The method of preparation was first published in London in 1724 by Woodward.[2] On reading over these interesting communications one must conclude that the method of preparation as then carried out differed but little in the main from that which is employed at present. The blue colour, ferric ferrocyanide, is still made on a large scale by adding together solutions of potassium ferrocyanide and ferric chloride.

A different method of preparation is also often followed in which one proceeds from white ferrous ferrocyanide, which is subsequently oxidised, to ferric ferrocyanide by chlorine or in some other way. By causing the precipitation and oxidisation to take place under different circumstances, many shades can be obtained which are on the market under various names.

The colouring power of the pigment is extraordinarily great; its state of division in oil is extremely fine, and on microscopic examination no separate particles can be recognised, so that one gets the impression, as with indigo, that the paint has dissolved in the oil. The two pigments do indeed

[1] Hermann Kopp, *Geschichte der Chemie*, Berlin, 1847, part iv. p. 369.

[2] *Philosophical Transactions*, 1724, vol. xxxiii. p. 15, *Praeparatio Caerulei Prussiaci ex Germaniâ missa ad Johannem Woodward.*

give the same appearance under the microscope, but there is chemically a marked difference in that Prussian blue is quickly attacked by dilute alkali, by which indigo is not affected. The conversion of the blue colour into brown can be easily followed, so that it is not possible to confuse the two pigments. Furthermore, when the concentration is not too small the Prussian blue can be re-formed by the addition of an excess of acid.

Prussian blue at the present time not only occupies an important place as a pigment, but is also employed in numerous mixtures, particularly green ones.

In order to obtain light-blue colours it can also be mixed with various fillings—for example, barium sulphate—and in this condition the pigment possesses a greater covering-power than the unmixed form has.

The lasting properties of Prussian blue are on the whole very high; on its being subjected to atmospheric influences, however, a decomposition of the pigment often occurs, which is accompanied by the formation of a metallic lustre with which the colours of thin films are sometimes also to be seen.

The 5 *specimens analysed, which are mentioned below, show that Prussian blue was first used in Holland in the second half of the* 18*th century.*

1770. *J. E. la Fargue. (G.) *The Binnenhof at the Hague.*
1774. P. C. la Fargue. (G.) *View of the Haagsche Schouw.*
1803. W. Hendriks. (G.) *Portrait of P. van Brussel.*
1806. A. Schelfhout. (G.) *Landscape.*
1816. J. H. Koekkoek. (Midd. 108.) *Digging the New Harbour at Middelburg.*

CHAPTER III

WHITE PIGMENTS

¶ White Lead

The oldest recipes[1] which have been given for the preparation of this pigment are in principle the same as those which are followed in the methods of preparation at present in use.

The well-known "stack" or Dutch process still furnishes a product of very good quality; it consists of subjecting thin lead sheets to the combined action of acetic acid vapour, oxygen, water vapour and carbon dioxide, the last two of which are generally obtained by the putrefaction of organic materials. The composition of white lead agrees approximately with the formula $2PbCO_3 . Pb(OH)_2$.

White lead has been employed to a considerable

[1] The *Secret Book* mentions the following recipe on p. 224:

"Hoe datmen Lootwit, ofte Ceruse maken sal."

"So verre als ghy selve wilt Loodwit maken so neemt loyenplaten | en hangtse in eenen verloyde pot | daer in dat goeden witten Wijnazijn sy | stopt den pot boven dichte toe | stelt hem op een warme plaetse | vier ofte vijf weken lanck | Neêt daer naer het Loot uit den Pot | ende schrabt de Materie oft het Loodwit daer vâ. Hanget alsdan wderom daer in | stopt het toe als voren. Hanghet dan wederom daer in | stopt hem toe als voren. Hanghet dan wederom daer in stopt den Pot als voren en schrabbet daer naer | alle 14 dagen eens | als voren | so hebdy goet Lootwit."

("How to make White Lead or Ceruse."

"If you wish to make white lead yourself, then take lead plates and hang these in an enamelled pot with good white vinegar, shut the pot at the top and set it in a warm place for four or five weeks. Then take the lead from the pot and scrape the matter or white lead therefrom. Then hang it again and shut it up as before. Scrape it afterwards every fourteen days; then you obtain good white lead.")

extent even from the very earliest days of painting, both as a simple pigment to supply the indispensable "light" required in a picture, and in mixtures with other pigments to obtain light shades. Its use has thus been very extensive and still is so at the present day, and it is no doubt due to the excellent keeping properties of this pigment that the paintings of former ages are still in such a good condition.

The pigment has a very great covering-power, and when ground in oil dries particularly quickly. The latter property is a consequence of the formation of a small amount of a drier, in this case a lead soap which is formed from the white lead and the free fatty acids in the oil. Consequently the drying also takes place quickly throughout the whole layer and forms a very resistant whole. This property is also retained by mixtures of it and other pigments. White lead is also excellently suited for use as an underpainting, and overpaintings or glazings will readily become firmly attached to it, for which reason white lead is very often employed as a priming, either alone or mixed with other substances.

When specimens of white lead are examined under the microscope a separate grain can only very seldom be recognised; in general the specimen will consist of a strongly coherent whole which with any thickness appears to be completely opaque.

If one observes the separate grains, which have very small dimensions, one may notice their transparency at the same time, and it is then possible to determine the refractive index by employing a greater magnification. This appears to be very high—above that of methylene iodide ($n = 1{\cdot}74$). Further, the double refraction of the separate grains

can be shown by examining them in polarised light between crossed nicols.

On account of the very general occurrence of white lead it is of importance to apply a simple test which can give an immediate indication of the identity of the pigment and at the same time, if possible, give directly the difference from other white pigments. Such a test is to be found in the treatment with dilute nitric acid in which the pigment dissolves with effervescence. When it is warmed and afterwards allowed to cool, the lead nitrate crystallises out in a characteristic form (Plate 14). For the further identification of the lead it is evaporated to dryness and taken up in acetic acid, and the triple nitrite reaction is carried out (Plate 6). Neither the poisonous properties of white lead nor its susceptibility to attack by hydrogen sulphide have stood in the way of its extensive use.

In general the envelopment of the pigment by oil appears to be a sufficient protection against both drawbacks.

It appears from the following list of 82 *specimens analysed that white lead has been in general use throughout all the ages.*

1437. Jan van Eyck. (A. 410.) *Saint Barbara.*
1450. *Rogier van der Weyden. (A. 393.) *The Bloodless Offering of the New Covenant, Symbol of the Bloody Offering of Golgotha.*
1490. *Hans Memling. (A. 780.) *Angels playing various instruments.*
1500. *Hieronymus Bosch. (A. 840.) *Our Saviour mocked by the Soldiers.*
1500. *Benson. (A. 262.) *The "Deipara Virgo" announced by Prophets and Sibyls.*
1509. Quinten Metsijs. (A. 246.) *The Entombment of Our Lord.*

1510. *Antwerp Master. (A. 385.) *Jesus in the midst of the Scribes.*
1510. *Antwerp Master. (A. 385.) *Jesus in the midst of the Scribes.*
1515. Jacob Cornelisz van Oostzanen. (A. 524.) *The Donor.*
1515. Jacob Cornelisz van Oostzanen. (A. 525.) *The Donor's Wife.*
1515. *Jan Provost. (A. 838.) *The Martyrdom of Saint Catherine.*
1525. Barend van Orley. (A. 741.) *The Last Judgment and the Seventh Work.*
1530. *Jan Swart. (A. 207.) *The Adoration of the Kings.*
1530. *Bruges Master. (A. 535.) *The Holy Virgin.*
1540. *School Engebrechtsz. (A. 532.) *Before the Crucifixion.*
1540. *Master of the Northern Part of the Netherlands. (A. 557.) *The Sibyl predicting the Birth of Christ to the Emperor Augustus.*
1550. *Jan van Eyck. (Copy, A. 412.) *Saint Mary, Saint George & Saint Donace, with the Donor, Joris van der Paele.*
1564. Jan Metsijs. (A. 252.) *Tobias receiving back his Sight.*
1570. *Master of the South Netherlands. (A. 548.) *Mater Dolorosa.*
1590. *Ambrosius Francken, the Elder. (A. 573.) *Christ in the Tomb.*
1600. *Wyttewaal. (M. 223.) *Mars and Venus.*
1600. *Jan van Eyck. (Copy, A. 415.) *The Holy Pilgrims.*
1600. *Pieter Breughel, the Elder. (Copy, A. 776.) *The Census of Bethlehem.*
1607. Pieter Breughel, the Younger. (A. 31.) *The Bearing of the Cross.*
1610. *Pieter Breughel, the Younger. (A. 644.) *Flemish Fair.*
1610. *Pieter Breughel, the Elder. (Copy, A. 777.) *The Sermon on the Mount.*
1610. *Hendrik Pot. (M. 475.) *A Merry Party.*
1614. Rubens. (A. 709.) *Venus Frigida.*
1615. *Rubens. (A. 319.) *Christ wept over by Saint John and the Holy Women.*
1615. *Rubens. (A. 312.) *Our Lady with the Parrot.*
1616. Frans Hals. (F.H. 123.) *Banquet of Officers of the Civic Guard of St. George.*
1620. *Rubens. (Copy, A. 315.) *The Descent from the Cross.*
1620. *Jacob Jordaens. (A. 844.) *Meleager and Atalanta.*

1627. Van Dyck. (A. 402.) *Jan Malderus, Fifth Bishop of Antwerp.*
1627. Dutch School. (F.H. 421.) (Underpainting.) *Portrait of Anna Dircksdr. van Bleyswijk.*
1627. Dutch School. (F.H. 421.) (Overpainting.) *Portrait of Anna Dircksdr. van Bleyswijk.*
1627. Frans Hals. (F.H. 125.) *Banquet of Officers of the Civic Guard of St. Adrian.*
1627. Frans Hals. (F.H. 124.) *Banquet of Officers of the Civic Guard of St. George.*
1630. *Van Dyck. (A. 407.) *Portrait of a Little Girl.*
1630. *Van Dyck. (A. 403.) *Christ taken from the Cross.*
1630. *Salomon van Ruysdael. (M. 566.) *Landscape.*
1633. Frans Hals. (F.H. 126.) *Assembly of Officers of the Civic Guard of St. Adrian.*
1635. Van Dyck. (A. 404.) *Christ in the Grave.*
1639. Frans Hals. (F.H. 127.) *Officers and Subalterns of the Civic Guard of St. George.*
1640. *Van Goyen. (M. 674.) *A Riverside Town.*
1640. *Hecken. (R. 1119.) *The Butcher's Shop.*
1640. *Lapp. (M. 84.) *Italian Landscape.*
1644. Van der Laeck. (G.) *The Nieuwberg Mansion.*
1647. Anth. Palamedesz. (R. 1837 a.) *A Guardroom with Soldiers.*
1650. *Jan Steen. (G.) *The Riviervischmarkt at the Hague.*
1650. *Quinten Metsijs. (Copy, A. 565.) *The Virgin embracing the dead Christ.*
1650. *Lingelbach. (M. 87.) *The Hay-harvest.*
1650. *Verbeecq. (M. 611.) *Two Horsemen near a Brook.*
1654. Jan Victors. (R. 2553 a.) *The Grocer's Shop, "de Buyskool."*
1657. Fonteyn. (R. 932.) *The Mosseltrap at Rotterdam.*
1658. Bega. (M. 400.) *Tavern Scene.*
1660. *Van der Helst. (M. 545.) *Portrait of a Young Lady.*
1660. *Ochtervelt. (M. 195.) *The Fish-seller.*
1660. *Vertangen. (G.) *Arcadian Landscape.*
1663. Van der Croos. (G.) *A View of the Hague.*
1663. Van der Croos. (G.) *A View of the Hague.*
1664. Frans Hals. (F.H. 129.) *Guardians of the Almshouses for Old Men.*
1664. Frans Hals. (F.H. 130.) *Lady Guardians of the Almshouses for Old Men.*

1664. Frans Hals. (F.H. 130.) *Lady Guardians of the Almshouses for Old Men.*
1665. Hanneman. (G.) *Portrait of Elizabeth van Limborgh.*
1670. *Willem van de Velde. (M. 471.) *The Surrender of the English Flag-ship "Royal Prince".*
1671. Vaillant. (R. 2341.) *Portrait of Maria van Oosterwyck.*
1671. Backer. (R. 397.) *Portrait of Daniel Niëllius.*
1693. Ludolf Bakhuysen. (M. 7.) *A Dutch Harbour.*
1702. Ludolf Bakhuysen. (R. 409 f.) *The Families Bakhuysen and de Hooghe.*
1707. Ludolf Bakhuysen. (R. 418.) *A Painter in his Studio at work on a Lady's Portrait.*
1710. *Van Huysum. (M. 71.) *Flowerpiece.*
1750. *Ten Compe. (G.) *The Plein at the Hague.*
1770. *J. E. la Fargue. (G.) *The Binnenhof at the Hague.*
1774. P. C. la Fargue. (G.) *A View on the Haagsche Schouw.*
1780. *Schweickhardt. (M. 669.) *A London Fruit-Merchant.*
1806. A. Schelfhout. (G.) *Landscape.*
1810. *J. F. Valois. (G.) *The Mauritshuis at the Hague.*
1816. J. H. Koekkoek. (Midd. 108.) *Digging the New Harbour at Middelburg.*
1840. *B. J. van Hoven. (G.) *The Heerengracht at the Hague.*
1848. A. Wijnantsz. (G.) *The Gothic Hall at the Hague.*
1860. *L. J. Kleyn. (G.) *A View of the Hague.*

¶ Zinc White

Although the possibility that in the use of zinc as a metal small quantities of zinc oxide were obtained accidentally is certainly not excluded, the first attempts to use the oxide as a pigment to replace white lead took place at the end of the 18th century.

Attention was directed by Courtois of Dijon in 1779 to the use of zinc carbonate and zinc oxide as pigments to replace white lead.[1] The experiments were continued in 1783 by Guyton de Morveau, who proved

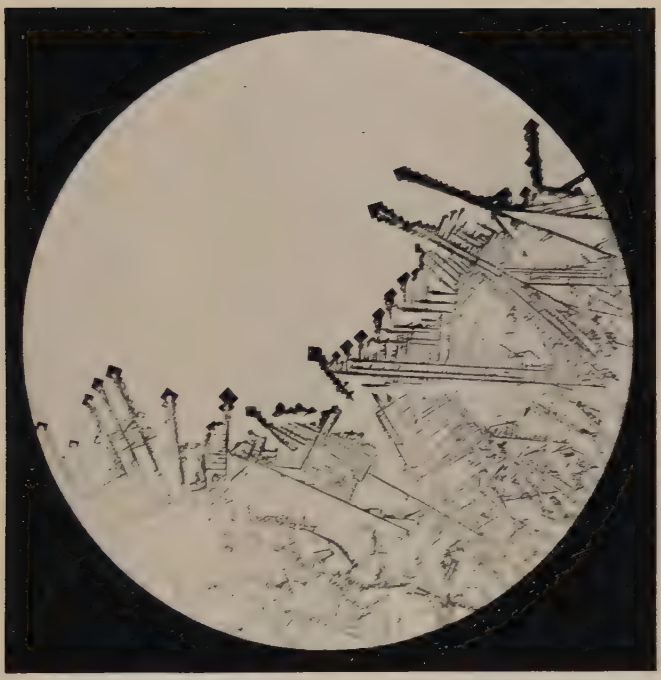
[1] Guignet, *Fabrication des couleurs*, Paris, 1888, p. 42.

that zinc oxide spread out as a paint underwent no change in colour under the influence of hydrogen sulphide, in contrast to white lead. Yet the less suitable properties of zinc white as a paint were also discovered at the same time. The covering-power appeared to be less than that of white lead and it dried very slowly.

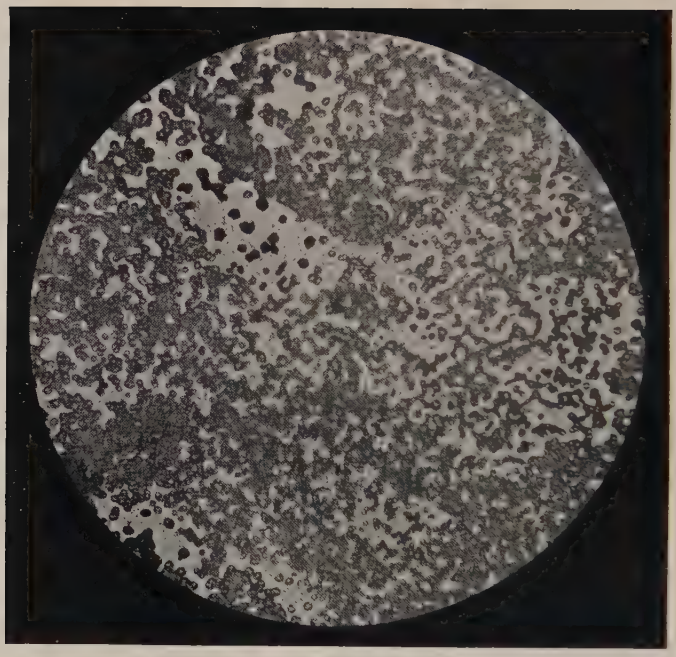
It seems that afterwards a few more experiments were carried out on a small scale, but that the pigment was otherwise quite forgotten until it was first prepared on a commercial scale by Leclaire in 1849. He also solved the problem of the slow drying by adding suitable driers to the oil. It is only since this date that there has been any question of a more general use of the pigment, and according to a communication from the firm of Hafkenscheid of Amsterdam the first trial orders for zinc white date from the beginning of 1854. Meanwhile it appears that zinc white was manufactured on a modest scale at an earlier date in England; at any rate it is mentioned with a certain amount of appreciation by Field,[1] and according to Church[2] it was put on the market as early as 1834 by Winsor & Newton of London under the name of "Chinese white".

Two processes for its production on a commercial scale can be distinguished, which are known as the direct and the indirect method. The first, also called the French method, proceeds from metallic zinc, which is burned in the vapour state at about 950°, after which the zinc oxide which forms is collected in suitable dust-collectors. The second method starts

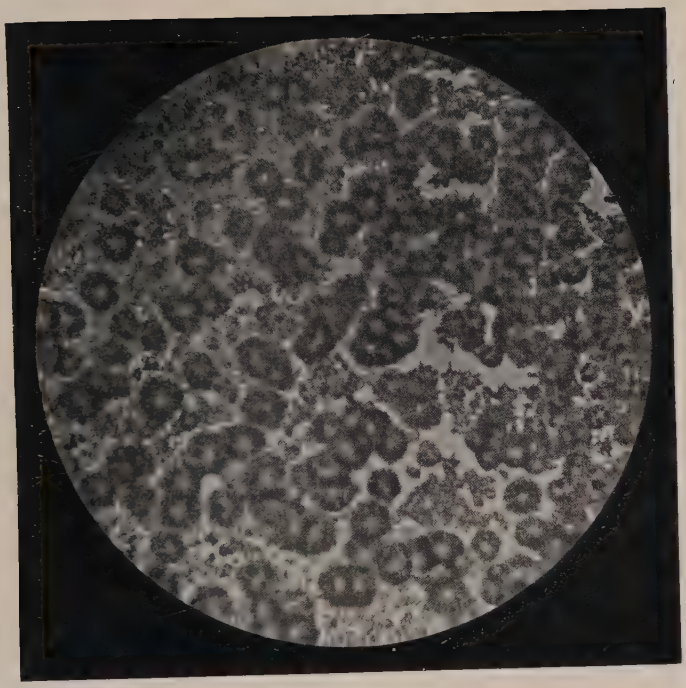
[1] *Chromotography*, 1835, p. 70.
[2] *The Chemistry of Paints and Painting*, 1915, p. 153.



14. LEAD NITRATE (42×)



15. ANHYDROUS ZINC NITRATE (105×)



16. ZINC NITRATE (105×)

The same specimen after water absorption

directly from the zinc ores and is principally used in America.[1]

Its non-poisonous nature and the fact that its colour is not altered by hydrogen sulphide are both properties which distinguish zinc white favourably from white lead, but in spite of these the latter has by no means been displaced by it.

In covering-power zinc white is inferior to white lead, especially as it requires a larger amount of oil (15 and 6 per cent by weight respectively)[2] to grind it to a consistency such that it can be spread out. In comparing the covering-power one deals with equal volumes of ground paint in practice. If, however, one chooses equal weights, the covering-powers are practically equal.[3]

On microscopic examination it is very difficult in practice to distinguish zinc white from white lead when no separate grains can be observed. If these are actually present, then zinc white does not appear to be doubly refractive, in contradistinction to white lead. The grains are, however, of very small dimensions in both cases and of the same shape.

The refractive index of zinc white is below that of methylene iodide ($n = 1{\cdot}74$).

When zinc oxide is dissolved in dilute nitric acid and then quickly evaporated, the zinc nitrate formed remains behind in the anhydrous state in the form of little spheres (Plate 15).

[1] See Dalton B. Faloon, *Zinc Oxide*, New York, 1925; R. G. Daniels, *Some Notes on the Manufacture of Zinc Oxide*, *Journal of the Oil and Colour Chemists' Association*, 1928, No. 98, vol. xi. p. 277.

[2] Morell and de Waele, *Rubber, Resins, Paints and Varnishes*, 1921, p. 118.

[3] Gentele, *Lehrbuch der Farbenfabrikation*, Braunschweig, 1909, part ii. p. 118.

On continuing the examination, for preference between crossed nicols, one observes that the anhydrous zinc nitrate is transformed into $Zn(NO_3)_2.6$ aq under the influence of the water vapour in the atmosphere, which transformation is characterised by the changing of the spheres into a complex of rosettes (Plate 16). These appear to show double refraction, which is not the case with the anhydrous spheres.

Further to confirm the presence of zinc, the whole is taken up in acetic acid and is acted on with ammonium-mercuric-thiocyanate, the corresponding zinc compound then crystallising out (Plate 17).

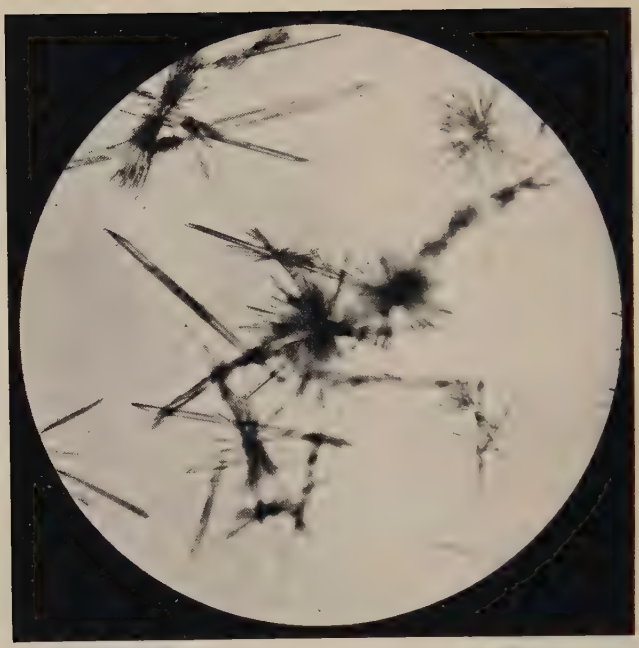
All the specimens of white paint were tested for zinc, but without exception with negative result.
From this it must be concluded with certainty that the use of zinc white agrees with the data furnished by information as to the history of this pigment.

¶ Whiting (Chalk)

This naturally occurring form of calcium carbonate has not to be taken into consideration as an oil-paint, but it is an important constituent in the preparation of priming. At various places whiting is to be found in a relatively pure state, and after being ground and carefully elutriated it is suitable for being worked up further.

On mixing whiting and oil one can only obtain a stiff plastic mass which cannot easily be spread out with a brush as one is accustomed to do with oil-paint. If one adds more oil, then the mass becomes thinly liquid fairly suddenly, but it can then be spread

17. ZINC-MERCURIC-THIOCYANATE (105×)



18. GYPSUM (105×)

out just as little, since it has a great tendency to trickle down. On being mixed with oil, whiting immediately loses its white colour and the mixture is coloured yellow as a consequence of the low refractive index of whiting ($n = 1{\cdot}60$).

By mixing whiting with a solution of glue (size) a very good plastic mass is obtained, which, though it cannot be spread with a brush, can very easily be worked with a spatula. It is in this form that whiting is employed as a priming-layer, which forms a very good foundation for the painting.

It is only after drying that one can rub in oil on this foundation and saturate it therewith, this being done because otherwise there is a chance that the oil from layers of oil-paint put on later would be abstracted by being absorbed in the foundation. One can also, instead of this, mix the whiting with a little white lead ground in oil.

With large magnifications the organic origin of the whiting particles can actually be recognised. The demonstration of the existence of double refraction, which is much stronger than with white lead, is, however, a much more definite way of identifying whiting.

Solution takes place very readily in acids with effervescence, and the calcium can be detected in the liquid so obtained by adding a little dilute sulphuric acid, whereby the characteristic crystals of gypsum are formed (Plate 18).

Since the above-mentioned white pigments occur not only separately but also mixed with each other, it is of importance to be able to detect all three in the same specimen of paint in some simple way.

An examination between crossed nicols immediately gives an indication of whiting or white lead. Next it is dissolved in dilute nitric acid and the liquid divided into three parts, in which white lead, zinc white and chalk (whiting) are successively demonstrated in the manner described above.

If zinc white is present together with much white lead some confusion may be produced in testing for zinc with ammonium-mercuric-thiocyanate through the corresponding lead compound crystallising out, since some forms of this latter compound give the impression of being the zinc compound. If there is thus a doubt, it is advisable first to remove the lead, which can be most easily done by precipitating it as sulphate. The liquid is then decanted off and the excess of sulphuric acid is removed by ignition, after which the specimen is taken up in acetic acid and the tests for zinc then follow in the usual manner.

There is also the possibility that gypsum has been used as well as chalk in the preparation of the priming. If this is probable, the specimen can be warmed with water, whereupon the gypsum dissolves to some extent, and after a little while the edge of the solution where evaporation has taken place is observed and will then be found to consist of needles of gypsum (Plate 18).

The following list of 36 *specimens of whiting shows that the substance universally occurred in primings throughout all times.*

Gypsum could not be detected in any of these cases.

1437. Jan van Eyck. (A. 410.) *Saint Barbara.*

1450. *Rogier van der Weyden. (A. 393.) *The Bloodless Offering of the New Covenant, Symbol of the Bloody Offering of Golgotha.*

1490. *Hans Memling. (A. 780.) *Angels playing various instruments.*
1500. *Benson. (A. 262.) *The "Deipara Virgo" announced by Prophets and Sibyls.*
1500. *Albrecht Bouts. (A. 223.) *The Adoration of the Shepherds.*
1500. *Hieronymus Bosch. (A. 840.) *Our Saviour mocked by the Soldiers.*
1509. Quinten Metsijs. (A. 246.) *The Entombment of Our Lord.*
1510. *Antwerp Master. (A. 385.) *Jesus in the midst of the Scribes.*
1515. *Jan Provost. (A. 838.) *The Martyrdom of Saint Catherine.*
1525. Barend van Orley. (A. 741.) *The Last Judgment and the Seventh Work.*
1530. *Bruges Master. (A. 535.) *The Holy Virgin.*
1530. *Jan Swart. (A. 207.) *The Adoration of the Kings.*
1540. *School Engebrechtsz. (A. 532.) *Before the Crucifixion.*
1540. *Master of the Northern Part of the Netherlands. (A. 557.) *The Sibyl predicting the Birth of Christ to the Emperor Augustus.*
1550. *Marinus van Reymerswael. (A. 244.) *The Tax-gatherers.*
1550. *Jan van Eyck. (Copy, A. 412.) *Saint Mary, Saint George and Saint Donace, with the Donor, Joris van der Paele.*
1564. Jan Metsijs. (A. 252.) *Tobias receiving back his Sight.*
1570. *Master of the South Netherlands. (A. 548.) *Mater Dolorosa.*
1590. *Ambrosius Francken, the Elder. *Christ in the Tomb.*
1600. *Jan van Eyck. (Copy, A. 415.) *The Holy Pilgrims.*
1600. *Pieter Breughel, the Elder. (Copy, A. 776.) *The Census at Bethlehem.*
1601. Marten de Vos. (A. 83.) *The Tribute to Caesar.*
1607. Pieter Breughel, the Younger. (A. 31.) *The Bearing of the Cross.*
1610. *Pieter Breughel, the Younger. (A. 797.) *The Adoration of the Kings.*
1610. *Pieter Breughel, the Younger. (A. 644.) *Flemish Fair.*
1610. *Pieter Breughel, the Elder. (Copy, A. 777.) *The Sermon on the Mount.*
1614. Rubens. (A. 709.) *Venus Frigida.*

1615. *Rubens. (A. 312.) *Our Lady with the Parrot.*
1620. *Jacob Jordaens. (A. 844.) *Meleager and Atalanta.*
1620. *Rubens. (Copy, A. 315.) *The Descent from the Cross.*
1627. Van Dyck. (A. 402.) *Jan Malderus, fifth Bishop of Antwerp.*
1627. Dutch School. (F.H. 421.) *Portrait of Anna Dircksdr. van Bleyswijk.*
1630. *Van Dyck. (A. 403.) *Christ taken from the Cross.*
1650. *Lingelbach. (M. 87.) *The Hay-harvest.*
1774. P. C. la Fargue. (G.) *View at the Haagsche Schouw.*
1816. J. H. Koekkoek. (Midd. 108.) *Digging the New Harbour at Middelburg.*

CHAPTER IV

YELLOW AND BROWN PIGMENTS

Besides the use of white lead, the employment of pure yellow pigments plays an important part in depicting the necessary "light" in a picture. Karel van Mander[1] accurately records which yellow pigments were used in his time. He says:

> "Maar wy hebben nu wel al vier verscheyden
> Ghelen boven ten Oker in ons tenten,
> Masticot, schiet-gheel, en twee Opramenten."

("But we now have four different yellows besides ochre at our disposal, massicot, yellow lake and two orpiments.")

These pigments are similarly mentioned by Samuel van Hoogstraeten[2] and Wilhelmus Beurs,[3] so that one can assume that these were the only yellow pigments which were used by the old Dutch painters.

¶ Massicot

The employment of massicot as a pigment is as old as that of white lead. When carefully heated to about 300° white lead is decomposed, and one obtains lead oxide with a fairly pure yellow colour.

$$2PbCO_3 . Pb(OH)_2 = 3PbO + 2CO_2 + H_2O.$$

This yellow form of PbO is, according to Ruer,[4] stable above 620°, while below this temperature a red-brown form is stable. The transformation of the

[1] *Het Schilder-Boeck*, Haarlem, 1604, 14th chapter.

[2] *Inleyding tot de Hooge Schoole der Schilderkonst*, Rotterdam, 1678, p. 220.

[3] *De Groote Waereld in 't kleen geschildert*, Amsterdam, 1692, part iii. p. 12.

[4] *Zeitschrift für anorganische Chemie*, 1906, part l. p. 265.

yellow into the red-brown form is, however, so slow that the yellow PbO must be reckoned among the stable substances in practice.

It does not yet seem to be settled whether we have to do in this case with two modifications or whether the difference in colour is a question of the state of division of the particles.[1]

Massicot, used as an oil-paint, has the same desirable properties as white lead. It possesses a well developed covering-power and by catalytic action brings about a rapid drying of the oil, so that it was perhaps not always easy to paint with it.[2]

On being examined under the microscope a specimen of massicot has a great resemblance to one of white lead. Separate grains can only rarely be recognised, and the specimen is generally a coherent whole which is completely opaque. The separate grains, which appear to be of very small dimensions and without any recognisable crystalline form, possess a refractive index above that of methylene iodide ($n = 1{\cdot}74$). The detection of lead is what identifies massicot; the specimen of paint is, for this purpose, treated with nitric acid, whereby solution takes place directly and lead nitrate crystallises out after slight evaporating of the excess of the acid (Plate 14). After evaporating to dryness, it is taken up in acetic acid and the triple nitrite reaction carried out (Plate 6).

[1] See in this connection: Germs, *Zeitschrift für anorganische Chemie*, 1921, part 119, p. 145; Glasstone, *Journal of the Chemical Society*, 1921, part 119, pp. 1689 and 1914; Appleby & Reid, *Journal of the Chemical Society*, 1922, part 121, p. 2129.

[2] Karel van Mander in *Het Schilder-Boeck*, Haarlem, 1604, 12th chapter, says: ". . . En quaet te verwercken door 't haestich drooghen". (". . . And difficult to work on account of the rapid drying".)

One can apply a further check by transforming massicot, PbO, into lead peroxide, PbO_2. This can be carried out in a suitable manner by fusing the specimen of paint on the corner of a microscopic slide with a small grain of potassium chlorate. One will then clearly observe in reflected light, after moistening with water, how the yellow colour of massicot is replaced by the brown one of lead peroxide.

Massicot has not an intense yellow colour, and strongly coloured green tints cannot be obtained by mixing it with blue pigments.

From the following list of 39 specimens of massicot investigated, it appears that this pigment was used very generally during the 15th, 16th and 17th centuries.

1450. *Rogier van der Weyden. (A. 393.) *The Bloodless Offering of the New Covenant, symbol of the Bloody Offering of Golgotha.*
1490. *Hans Memling. (A. 780.) *Angels playing various instruments.*
1500. *Albrecht Bouts. (A. 233.) *The Adoration of the Shepherds.*
1509. Quinten Metsijs. (A. 245.) *St. John the Baptist Beheaded.*
1510. *Antwerp Master. (A. 385.) *Jesus in the midst of the Scribes.*
1515. *Jan Provost. (A. 838.) *The Martyrdom of Saint Catherine.*
1515. Jacob Cornelisz van Oostzanen. (A. 523.) *The Virgin Mary and the Christ-Child.*
1530. *Jan Swart. (A. 207.) *The Adoration of the Kings.*
1530. *Bruges Master. (A. 535.) *The Holy Virgin.*
1540. *Master of the Northern Part of the Netherlands. (A. 557.) *The Sibyl predicting the Birth of Christ to the Emperor Augustus.*
1540. *School Engebrechtsz. (A. 532.) *Before the Crucifixion.*
1550. *Jan van Eyck. (Copy, A. 412.) *Saint Mary, Saint George and Saint Donace, with the Donor, Joris van der Paele.*

1550. *Benson. (Copy, A. 264.) *A Noblewoman.*
1564. Jan Metsijs. (A. 252.) *Tobias receiving back his Sight.*
1590. *Ambrosius Francken, the Elder. (A. 573.) *Christ in the Tomb.*
1600. *Wyttewaal. (M. 223.) *Mars and Venus.*
1600. *Pieter Breughel, the Elder. (Copy, A. 776.) *The Census at Bethlehem.*
1601. Marten de Vos. (A. 83.) *The Tribute to Caesar.*
1607. Pieter Breughel, the Younger. (A. 31.) *The Bearing of the Cross.*
1610. *Pieter Breughel, the Younger. (A. 644.) *Flemish Fair.*
1610. *Pieter Breughel, the Younger. (A. 797.) *The Adoration of the Kings.*
1610. *Pieter Breughel, the Elder. (Copy, A. 777.) *The Sermon on the Mount.*
1610. *Pieter Breughel, the Elder. (A. 926.) *Landscape.*
1610. *Hendrik Pot. (M. 475.) *A Merry Party.*
1616. Frans Hals. (F.H. 123.) *Banquet of Officers of the Civic Guard of St. George.*
1620. *Rubens. (Copy, A. 315.) *The Descent from the Cross.*
1620. *Jacob Jordaens. (A. 844.) *Meleager and Atalanta.*
1627. Dutch School. (F.H. 421.) *Portrait of Anna Dirckdr. van Bleyswijk.*
1630. *Van Dyck. (A. 403.) *Christ taken from the Cross.*
1633. Frans Hals. (F.H. 126.) *Assembly of Officers of the Civic Guard of St. Adrian.*
1639. Frans Hals. (F.H. 127.) *Officers and Subalterns of the Civic Guard of St. George.*
1640. *Hecken. (R. 1119.) *The Butcher's Shop.*
1647. Anth. Palamedesz. (R. 1837 a.) *A Guardroom with Soldiers.*
1657. Fonteyn. (R. 932.) *The Mosseltrap at Rotterdam.*
1660. *Ochtervelt. (M. 195.) *The Fish-seller.*
1671. Vaillant. (R. 2341.) *Portrait of Maria van Oosterwyck.*
1671. Backer. (R. 397.) *Portrait of Daniel Niëllius.*
1702. Ludolf Bakhuysen. (R. 409 f.) *The Families Bakhuysen and de Hooghe.*
1707. Ludolf Bakhuysen. (R. 418.) *A Painter in his Studio at work on a Lady's Portrait.*

¶ Ochres

The natural yellow and brown earthy pigments are among the oldest products which have been employed in painting.

Four specimens of ancient Egyptian paints of different colours, from the Museum of Antiquities at Leiden, Holland, appeared to consist of yellow and red-brown ochre. It was thus probably known even at that time that the yellow colour can pass over into a red-brown on heating.

The ochres consist of various kinds of clay, which are coloured by the presence of varying amounts of hydrated iron oxide. Consequently their name is a collective one for a large number of differently coloured pigments which have the most diverse places of origin and names. It is also extended to the colours which can be obtained by heating the naturally occurring products. The places of origin are spread over all Europe, so that the ochres found extensive application in all the schools of painting.

The preparation of the natural product for use as a pigment is generally by grinding carried out and elutriating it, whereby the impurities are removed and at the same time products of different degrees of fineness are obtained. The finest are used for artistic purposes.

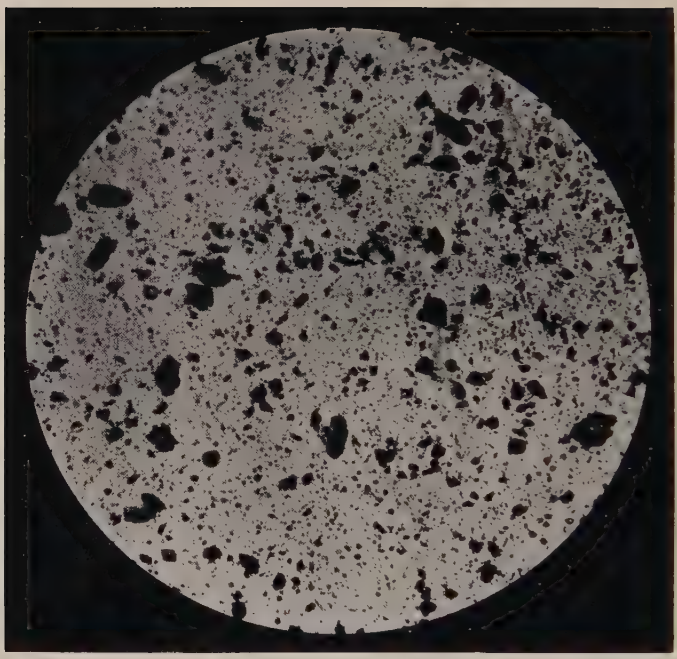
The ochres are, in general, very stable pigments and require an unusually large amount of oil to prepare them as oil paints. The amount can vary between 40 and 70 per cent of the total weight of the paint.[1] Consequently the ochres afford the most

[1] Calculated from Pettenkofer, *Über Ölfarbe*, Braunschweig, 1902, p. 11.

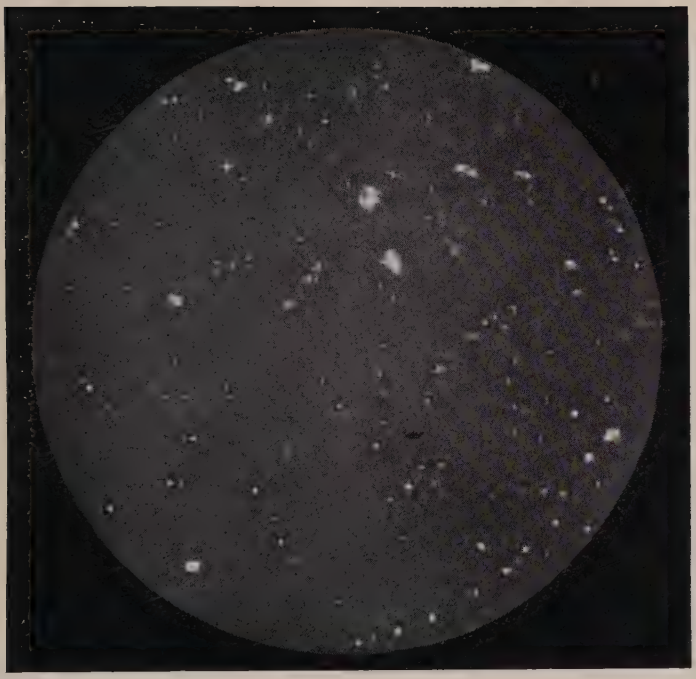
striking example of darkening. The oil undergoes a change of colour on drying, and the tint of the paint is thereby influenced. In proportion as the amount of the oil in a paint is greater this influence will make itself more felt; hence in this case the darkening of the colour is very readily observable. Naturally, this may vary with the different kinds of ochres, but it is generally clearly visible. The old retouchings on paintings which contain ochre can often be pointed out directly on account of this darkening; the difference in colour is sometimes so striking that one may ask oneself whether the part ever was repainted exactly in the surrounding colour.

The appearance of the ochres under the microscope (Plates 19 and 20) is, naturally, very heterogeneous. Particles of all sorts of colours and with different optical properties accompany each other; there is no question of a uniform product. Yellow and brown particles are, however, present to a large extent, besides many colourless or light-coloured ones.

These pigments are characterised by the presence of iron, which can be detected as Prussian blue after evaporating several times with strong hydrochloric acid or after igniting with concentrated sulphuric acid. The so-called umbers and raw sienna are also varieties of ochre. The former contain a small quantity of the oxides of manganese, as a result of which they dry fairly quickly. The manganese can be detected by fusing with a little soda and saltpetre (KNO_3). The latter contains a large quantity of the oxides of iron, and consequently has a brown to red-brown colour.



19. OCHRE (105×)



20. OCHRE (105×)

The same specimen between crossed nicols

The following list of 20 specimens of ochre investigated shows that its use has been maintained throughout all periods.

1515. *Jan Provost. (A. 838.) *The Martyrdom of Saint Catherine.*
1615. Rubens. (A. 312.) *Our Lady with the Parrot.*
1616. Frans Hals. (F.H. 123.) *Banquet of Officers of the Civic Guard of St. George.*
1620. *Jacob Jordaens. (A. 844.) *Meleager and Atalanta.*
1627. Van Dyck. (A. 402.) *Jan Malderus, fifth Bishop of Antwerp.*
1627. Frans Hals. (F.H. 125.) *Banquet of Officers of the Civic Guard of St. Adrian.*
1627. Frans Hals. (F.H. 124.) *Banquet of Officers of the Civic Guard of St. George.*
1630. *Van Dyck. (A. 407.) *Portrait of a Little Girl.*
1633. Frans Hals. (F.H. 126.) *Assembly of Officers of the Civic Guard of St. Adrian.*
1639. Frans Hals. (F.H. 127.) *Officers and Subalterns of the Civic Guard of St. George.*
1650. *Jan Steen. (G.) *The Riviervischmarkt at the Hague.*
1658. Bega. (M. 400.) *Tavern Scene.*
1664. Frans Hals. (F.H. 130.) *Lady Guardians of the Almshouses for Old Men.*
1702. Ludolf Bakhuysen. (R. 409 f.) *The Families Bakhuysen and de Hooghe.*
1710. *Van Huysum. (M. 71.) *Flowerpiece.*
1750. *Ten Compe. (G.) *The Plein at the Hague.*
1774. P. C. la Fargue. (G.) *View on the Haagsche Schouw.*
1810. *J. F. Valois. (G.) *The Mauritshuis at the Hague.*
1816. J. H. Koekkoek. (Midd. 108.) *Digging the New Harbour at Middelburg.*
1848. A. Wijnantsz. (G.) *The Gothic Hall at the Hague.*

¶ Yellow Lakes

In the 17th century, and perhaps even earlier, the extracts of a number of yellow-coloured flowers were used in colouring illuminated manuscripts. These

organic colouring matters appear also to have been precipitated on chalk or aluminium hydroxide, by which they obtained a certain covering-power and came to be used in oil painting.[1]

Although yellow lake appears in nearly all the old text-books on painting, its use seems, nevertheless, to have been very restricted, because experience has shown that the colouring matters were not at all stable under the action of light. The name of the pigment in Dutch (*schietgeel*) is perhaps to be attributed to this fact (*ver-schietgeel* = fading yellow). The fading of the yellow tint from some green parts on a painting causes them to turn blue. This can readily be observed, for example, in pictures by Vermeer, Pieter de Hoogh, Paulus Potter and others, where green foliage is now entirely blue.

Several specimens in the Hafkenscheid collection proved to be a yellow lake precipitated on chalk. When heated, the organic colouring matter burns while the chalk remains behind and can be detected by adding a little sulphuric acid after dissolving in nitric acid (Plate 18). When treated with ammonia the colouring matter appeared to be somewhat

[1] *Secreet-Boeck*, Dordrecht, 1609, p. 217. "Neemt Wauwe | diemen in lattijn noemt Flortinctorius, dat zijn de geluwe Blommen | die de Verwers gebruycken | neemt die met de stelen | en blommen onder een | soo veel alstublieft. Maekt een Calcwater | giet dat op de blommen in eenen grooten ketel | latet so lange sieden | tot dat de gheluwicheyt der blommen | uit mach sieden. . . ." ("Take as much as you will of the yellow flowers of the weed or dyer's weed, which in Latin is called Flortinctorius, with the stalks on them. Make up lime-water and pour that on the flowers in a large kettle and let it boil until the yellow colour of the flowers is boiled out.") . . . Mayerne MS., p. 122, verso, "Le Schitgeel ou Pinke peult aussi passer entre les terres parce que son corps est de craye, quoy que la teincture vienne de l'herbe Isatis (?) laquelle est précipitée auec l'allum puis paistris auec la craye."

soluble, so that a yellow-coloured edge developed when the solution was evaporated.

No yellow lake, precipitated on chalk, appeared to be present in the specimens of the yellow pigments investigated.

¶ Orpiment

In view of the small number of light-yellow pigments which was available in the old days, the use of this natural arsenic-sulphur compound As_2S_3 appears to have received but little attention. The cause of this must to a great extent be sought in its poisonous nature, which was certainly known at that time.[1] When a specimen of orpiment is simply heated, oxidation takes place at once; the arsenic trioxide which is formed sublimes very easily and can be condensed on a microscope slide. The characteristic octahedral form of the As_2O_3 crystals can then be recognised with large magnification.

The specimen of orpiment can also be heated directly with a little nitric acid. Crystals of arsenic trioxide of fairly large dimensions will then be visible at the edge of the solution.

[1] *Secreet-Boeck*, Dordrecht, 1609, p. 216. "Van het Orpigment. Dit is ooc een sorgelick (maer een schoone verwe). Als gy dat wrijft | soo stopt Neus | ende Mondt | op dat ghy noch den Domp | noch het Stof daer van niet int lijf en crijght. . . . Ende wacht u dat ghy geene Pinceelen van deze verwe en leckt want sy is seer schadelick. . . ." ("Of Orpiment. This is a dangerous but beautiful pigment. When you grind it, close the nose and mouth so that you get neither the vapour nor the dust into your body. . . . And take care that you do not lick any brushes containing this paint, for that is very dangerous. . . .") Karel van Mander in *Het Schilder-Boeck*, Haarlem, 1604, at the end of the 12th chapter, says: "En Orpimenten giftich van natueren". ("And Orpiments, which are naturally poisonous".)

When a specimen of orpiment is examined with the microscope the particles appear to possess a fibrous structure. The refractive index is above that of methylene iodide.

No orpiment was found in the specimens of yellow pigments which were investigated.

This agrees with the experience of Raehlmann.[1]

¶ Naples Yellow

Mention is made by as early a writer as Cennino Cennini[2] of a yellow pigment called "giallorino" which was of natural origin. This name has been attached to Naples yellow, but the pigments concerned are probably not identical. The first product is very likely a light kind of ochre which came from the neighbourhood of Naples. The latter is an artificially prepared pigment, originally also coming from Italy, which consists principally of lead antimoniate, $Pb_3(SbO_4)_2$.

The oldest recipes for the preparation of Naples yellow date from 1758 and were given by Passari,[3] who also mentions that various shades can be obtained. More accurate recipes were in addition given by Brunner.[4] By heating a mixture of potassium antimonyl tartrate, lead nitrate and sodium chloride till the last-mentioned substance melts and acts as a flux, one obtains, on cooling, a yellow mass, which furnishes a very stable pigment after washing and powdering.

[1] *Über die Farbstoffe der Malerei*, Leipzig, 1914, p. 233.
[2] *Trattato della pittura*, 1437.
[3] Dinglers *Polytechnisches Journal*, 1828, part 28, p. 225.
[4] Dinglers *Polytechnisches Journal*, 1837, part 63, p. 379.

The susceptibility to attack by hydrogen sulphide is smaller than with white lead; the covering-power is very good, and the pigment can be used in mixtures without objection.

A warning is given in various publications[1] against allowing the pigment to come into contact with iron, tin or zinc during the manufacture, as a dark discoloration may be produced. The most probable explanation of this is that, on account of its great hardness, Naples yellow simply acts as an abrasive and is altered in colour by the fine metallic particles of the metals with which it comes into contact.

When examined under the microscope (Plate 21) Naples yellow appears to be an extraordinarily finely divided pigment. No crystalline form can be detected even with high magnification. The refractive index is above that of methylene iodide, so that there is optically a great similarity to massicot. The sensitivity to attack by nitric acid is small, although evaporating several times with it has the consequence that lead can be detected by means of the triple nitrite reaction (Plate 6). This is, however, not a sharp distinction from massicot. Fusing the specimen of paint with a grain of potassium chlorate serves best for this purpose, as a result of which no change in colour takes place, whereas massicot turns brown on account of the formation of lead peroxide.

The detection of antimony further serves to characterise the pigment. When the specimen of paint is treated with a small amount of antimony-free zinc and a little hydrochloric acid, a trace of antimony

[1] Church, *The Chemistry of Paints and Painting*, 1915, p. 179; Weber, *Artist's Pigments*, 1924, p. 92.

hydride is formed and can be detected with a piece of filter paper soaked with a solution of silver nitrate.

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3.$$

It is simplest to carry out this reaction in the space obtained by placing two hollow-ground microscopic slides one on top of the other.

No Naples yellow was met with in the specimens of yellow pigments which were investigated.

This is in agreement with the statement of Field,[1] who says that Naples yellow was not used by the old masters.

The statement of Raehlmann[2] that he detected Naples yellow on paintings of the Renaissance period must be accepted with reserve, since the test he used (black coloration with sodium sulphide) is not characteristic.

The tubes of Naples yellow at present on the market generally contain a mixture of several other pigments which have the same colour : for example, white lead, yellow ochre, Venetian red (red ochre) and cadmium yellow—a mixture prepared by Messrs. Winsor & Newton.

¶ Chrome Yellow

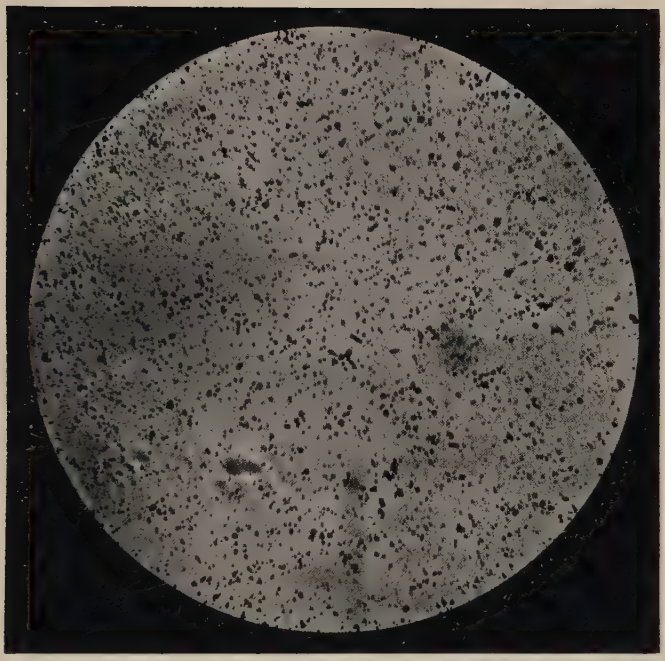
A series of investigations on Siberian red lead ore (krokoite), which were described by Hassenfratz,[3] were continued by Vauquelin,[4] who dissolved the

[1] *Chromotography*, 1835, p. 78.

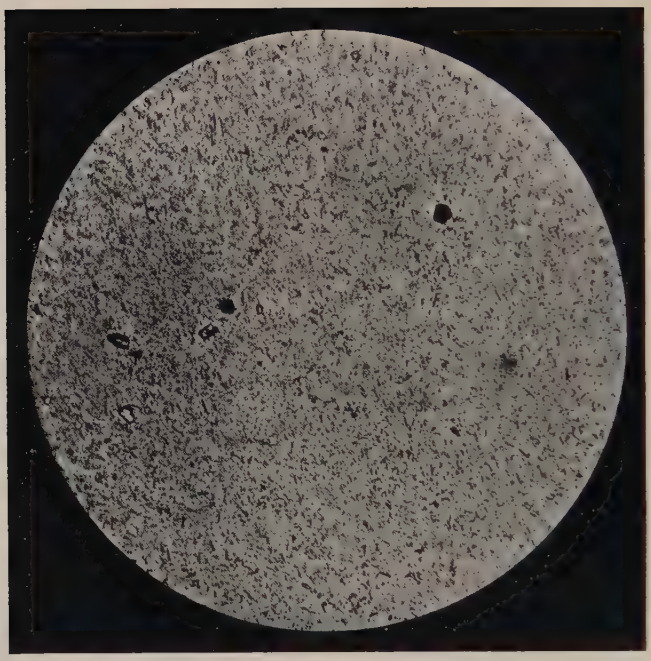
[2] *Über die Farbstoffe der Malerei*, Leipzig, 1914, p. 24.

[3] *Annales de chimie*, 1789, part 1, p. 300.

[4] *Annales de chimie*, 1798, part 25, p. 26. "Mémoire sur une nouvelle substance métallique contenue dans le plomb rouge de Sibérie et qu'on propose d'appeler Chrome, à cause de la propriété qu'il a de colorer les combinaisons où il entre."



21. NAPLES YELLOW (210×)



22. CHROME YELLOW (210×)

23. CHROME YELLOW (105×)

Crystals of Silver Chromate are growing out of the specimen

mineral in potassium hydroxide (KOH). He added to the solution one of lead nitrate, on which an intense yellow-coloured precipitate formed. By this means synthetic lead chromate was first prepared.

The strong yellow colour of this compound, which differed very much from that of any of the yellow pigments then in use, was the reason that the pigment came into general use relatively shortly after its discovery. It was, however, not before 1818 that there was any question of the commercial production of chrome yellow, when large quantities of chromate were more easily obtainable through the working up of chromite, $FeO \cdot Cr_2O_3$.[1] This manufacture is still carried out by adding together solutions of a chromate and lead nitrate or acetate. By carrying out the precipitation under different circumstances, one can obtain a number of different shades.

On microscopic examination lead chromate is seen to be a very finely divided pigment. With a larger magnification its crystalline character is clearly visible. The substance then appears to consist of very fine needles, which are doubly refractive (Plate 22) and possess a refractive index above that of methylene iodide.

This form is consequently very characteristic, and the most important remaining test for this pigment is the detection of the chromate. This can be carried out in a very simple manner by treating the specimen of paint cold with a little cold dilute nitric acid and putting a few grains of silver nitrate into this liquid.

After a short time one sees by reflected light the

[1] Guignet, *Fabrication des couleurs*, Paris, 1888, p. 98.

intensely red-coloured crystals of silver chromate growing everywhere out of the specimen of paint (Plate 23). The reaction can be followed very clearly from the beginning, and on account of the strong contrast in colour it certainly must be reckoned among the most beautiful tests which can be carried out. It is very important to allow the whole reaction to take place at room temperature since, with the least heating, the chromic acid set free oxidises the dried oil in the specimen of paint, as a result of which no silver chromate is formed.

Lead chromate is a paint of very good covering-power, which dries fairly quickly on account of the catalytic action of the lead. This property is also extended to the numerous mixtures in which lead chromate occurs.

It appears, however, that chrome yellow is not completely stable under all circumstances. Eibner[1] attributes this to reduction by sulphurous acid in the atmosphere, whereby a little green Cr_2O_3 is formed and the yellow colour changes to yellowish green. Brown discoloration also occurs under the influence of hydrogen sulphide through the formation of PbS. In both cases the enveloping oil has a protective action, so that chrome yellow finds extensive application.

This pigment was not found at all in the specimens of paint investigated, which, however, date chiefly from the times which preceded the discovery of lead chromate.

[1] *Malmaterialienkunde*, Berlin, 1909, p. 164.

¶ Cadmium Yellow

The discovery of this pigment was made almost simultaneously in 1818 by Stromeyer and Hermann.[1] In investigating specimens of zinc oxide they found that when hydrogen sulphide was passed through zinc oxide dissolved in acid, a yellow precipitate was formed. They were able to show that this was not due to any impurity of arsenic, but that the yellow colour had to be attributed to the sulphide of a new metal, which was given the name of cadmium.

The yellow compound was first recommended as a pigment by Melandri in 1829.[2]

Passing hydrogen sulphide through a solution of a cadmium salt can lead to the formation of differently coloured precipitates. By changing the degree of acidity of the solution or by varying the manner of passing the gas through the solution, one can obtain cadmium yellow ranging from a light yellow to a dark orange. The question whether this phenomenon must be ascribed to the occurrence of different modifications of CdS or to a different state of division of the particles does not seem to have been settled yet.

The appearance in a microscope with large magnification (1500 ×) is very characteristic and differs strikingly from that of other pigments. Cadmium yellow forms very fine grains, which are all transparent; for the greater part, however, they congregate together into flakes, which are strongly coloured and transparent, but are clearly seen to

[1] Kopp, *Geschichte der Chemie*, Berlin, 1847, vol. iv. p. 124.
[2] Munkert, *Die Normalfarben*, München, 1905, p. 47.

be built up of the above-mentioned small grains in which no crystalline form can be recognised.

The covering-power as an oil-paint differs somewhat with the different tints. The orange colours cover best; the lighter tints are consequently more suitable for glazing-paints.

These latter appear to be somewhat subject to a colour change. Church[1] has carried out some experiments on this point and attributed the bleaching of the light yellow cadmium sulphide to the action of oxygen and water vapour in the atmosphere. He could detect a little cadmium hydroxide in the bleached pigment.

The microchemical detection of cadmium sulphide is best performed on a specimen of paint by carrying out a test for cadmium. Evaporation with hydrochloric acid gives strongly doubly refractive needles of cadmium chloride. One puts a drop of a saturated solution of rubidium chloride on to the dry residue from the evaporation, after which rhombs of $RbCl.CdCl_2$ crystallise out.

By treating with zinc dust and hydrochloric acid the sulphur can also be detected if necessary.

No cadmium yellow was met with in the specimens of yellow pigments investigated.

¶ Gold

On account of its intense yellow colour, its high gloss and its absolute stability, gold leaf was a material particularly suitable for applying to surfaces to which it was desired to give a golden-yellow colour.

[1] *The Chemistry of Paints and Painting*, 1915, p. 165.

Only a small quantity of gold is required to cover a large surface, because the gold can be beaten into extremely thin leaves. Fixing to a foundation can be done with a slow-drying varnish or with a solution of egg white. In order to obtain a smooth surface it can be polished with an agate spatula or some other hard smooth object to which gold leaf does not stick. When it is examined under the microscope by reflected light, the strong metallic gloss is readily observed. It is identified by testing with thallium nitrate after dissolving in *aqua regia*, whereby lemon-yellow needles of $TlAuCl_4.5H_2O$ are formed.

Gold was found to be present in the 4 specimens mentioned below:

1450. *Rogier van der Weyden. (A. 393.) *The Bloodless Offering of the New Covenant, Symbol of the Bloody Offering of Golgotha.*

1490. *Hans Memling. (A. 780.) *Angels playing various instruments.*

1500. *Hieronymus Bosch. (A. 840.) *Our Saviour mocked by the Soldiers.*

1540. *Master of the Northern Part of the Netherlands. *The Sibyl predicting the Birth of Christ to the Emperor Augustus.*

¶ Mummy and Asphaltum

The first product was originally of Egyptian origin, though it is probable that a similar substance was also formerly prepared in Holland.[1] A specimen from the Museum of Antiquities at Leiden, Holland,

[1] *Secreet-Boeck*, Dordrecht, 1609, p. 224: "Men vint de Mommie nerghens als inde Apteke | het is van Menschenvleesch | dat Constich is gedrooght en bereyt." ("One finds Mummy only in the apothecary's shop; it is made from human flesh which is dried and prepared.")

proved on microscopic examination to consist of transparent brown flakes of diverse sizes, but without any structure. It becomes very finely divided in oil and then forms an excellent glazing-paint.

Various kinds of asphaltum also appear to have been employed in former times in oil-painting.[1] They become very finely divided in oil and can also be used as glazing-paints.

Both products when prepared as oil-paints dry particularly slowly in thick layers; the paint becomes covered at the beginning with a dry film under which no, or very slow, drying takes place. There are thus examples in modern paintings in which the paint was not yet dry after tens of years and still remained plastic.

When, however, a dryer is added to the oil, quicker drying will generally take place, but very unpleasant cracks may often occur in the paint-layer with these particular pigments. The 18th-century British school shows many pictures in which this defect can be noticed.

Both products, being of organic origin, can be completely combusted on a microscopic slide and leave behind only a trace of ash.

¶ Carbon Black

The use of a black pigment for giving the "darkness" in a picture is just as important as the white pigments for adding the necessary "light", and from the earliest periods of the art of painting, carbon has been universally employed for this purpose.

[1] Karel van Mander, *Het Schilder-Boeck*, Harlem, 1604, at the end of the 12th chapter mentions the use of various asphalts.

It was prepared in various ways. The purest, deepest black which covers well can be obtained from a smoking flame (lamp black) for which fat or oil was generally used formerly. In addition good kinds of carbon can also be obtained by carefully carbonising some parts of plants—peach stones, for example.[1] The kind most used was, however, the so-called bone-black, prepared by carbonising bones. On account of the presence of calcium phosphate the colour of this substance is not absolutely black, but the covering-power is greater than that of the purer kinds of carbon.

The appearance under the microscope of these products is that of an amorphous, completely opaque substance, which is finely divided.

For the purpose of identification one may simply heat the specimen of paint in the air, as a result of which the carbon burns completely, or, if necessary, fuse with a grain of potassium chlorate.

Since the use of carbon as a black paint will always continue, specimens of black were not collected.

[1] *Secreet-Boeck*, Dordrecht, 1609, p. 224: "Persesteenswart. So verre als ghy een schoon | en liefelic swart hebbe wilt. So neempt eenen goeden deel Persesteenen | doettet in eenen nieuwen pot | met een deksel daer op luteret boven dichte toe | datter geenen damp uit en mach | anders souden de steenen | geheel tot Asschen worden. Stelt desen pot also in een Potbackershove | laet he brande so lange als de ongebrande potten branden moete. Als hy nu gebrant heeft | so neet die swarte gebrande steene daer uyt. Stootse in eenen mortier wel cleyne | wrijftse daer naer op eene stee. . . ." ("Black from peach stones. If you would have a beautiful and good black, then take a number of peach stones and put these into a new pot with a lid and seal it tight on top, so that no vapour can pass out, otherwise the stones will be burned completely to ash. Put the pot in a potter's oven and heat it as long as the unburned pots must be baked. When now it is burnt, then take the black burnt stones out. Pound them in a mortar and grind them afterwards on a stone.")

CHAPTER V

RED PIGMENTS

¶ Vermilion

When natural cinnaber is pure it furnishes in powder form an excellent pigment which has been used in painting from the earliest times.

The preparation of vermilion from the elements mercury and sulphur is also of very ancient date. When the two elements are ground together the black modification of mercury sulphide, HgS, is formed. If this is subsequently heated, sublimation takes place, and on condensation one obtains the red modification.[1]

Both the natural product and that obtained by sublimation have a crystalline character when examined under the microscope. The pigment then has entirely the external appearance of a crumbled mineral, the particles of which are faintly doubly refractive and possess a refractive index above that of methylene iodide (Plate 24).

In 1687 Gottfried Schulz[2] succeeded in obtaining the red modification of mercury sulphide by treating the black modification with alkali sulphides. This method of preparation is also generally applied at the present time. The product obtained in this manner has a much finer grain, when examined under the microscope (Plate 25), than the pigment prepared by sublimation, but the optical properties are the same.

[1] The *Secreet-Boeck*, Dordrecht, 1609, mentions various recipes for the preparation of vermilion all based on the sublimation of black mercury sulphide.

[2] Kopp, *Geschichte der Chemie*, Berlin, 1847, vol. iv. p. 187.

24. NATURAL VERMILION (210×)

25. SYNTHETIC VERMILION (210×)

Although the two products, obtained by means of the dry and the wet method respectively, are chemically identical, a difference in stability nevertheless sometimes occurs. For instance, it may happen that the red vermilion undergoes an alteration in colour on the surface under the influence of light, this change showing itself in considerable darkening of the paint-layer. The transformation is probably that of the stable red modification into the metastable black form, which under ordinary conditions has its transition point at about 386°,[1] or a very small decomposition which disturbs the colour effect on the surface.

Various shades of vermilion can be obtained which have their origin in the different states of division. The sublimed product has a dark-red colour with a somewhat violet tint. The finer it is ground, the lighter the colour becomes; with the finest kinds it approaches orange. The pigment covers very well, but does not dry particularly quickly. It can be employed in mixtures without objection; even with white lead there is no danger of the formation of lead sulphide.

The black coloration under the influence of light may be considered exceptional when the pigment is employed as an oil-paint.

Microchemical confirmation of the presence of vermilion may be found in the detection of mercury. For this purpose the specimen of paint is evaporated several times with *aqua regia*, on which the vermilion dissolves and mercuric chloride is formed. One must take care not to heat too greatly, since the latter product easily sublimes.

[1] Rinse, *Recueil des travaux chimiques des Pays-Bas*, 1928, part xlvii. p. 28.

Care must also be taken that the dried oil does not envelop the mercuric chloride, since in that case no reaction takes place on the addition of ammonium thiocyanate and cobalt acetate, which follows.

The mercury sulphide is completely identified by the formation of cobaltous-mercuric-thiocyanate (Plate 10).

It is seen from the following list of 23 specimens of vermilion investigated that this pigment has been used throughout all times.

1450. *Rogier van der Weyden. (A. 393.) *The Bloodless Offering of the New Covenant, Symbol of the Bloody Offering of Golgotha.*
1490. *Hans Memling. (A. 780.) *Angels playing various Instruments.*
1500. *Benson. (A. 262.) *The "Deipara Virgo" announced by Prophets and Sibyls.*
1509. Quinten Metsijs. (A. 246.) *The Entombment of the Lord.*
1525. Barend van Orley. (A. 741.) *The Last Judgment and the Seventh Work.*
1550. *Marinus van Reymerswael. (A. 244.) *The Tax-gatherers.*
1564. Jan Metsijs. (A. 252.) *Tobias receiving back his Sight.*
1590. *Ambrosius Francken, the Elder. (A. 573.) *Christ in the Tomb.*
1601. Marten de Vos. (A. 83.) *The Tribute to Caesar.*
1607. Pieter Breughel, the Younger. (A. 31.) *The Bearing of the Cross.*
1610. *Pieter Breughel, the Elder. (Copy, A. 777.) *The Sermon on the Mount.*
1610. *Pieter Breughel, the Younger. (A. 644.) *Flemish Fair.*
1610. *Pieter Breughel, the Younger. (A. 797.) *The Adoration of the Kings.*
1614. Rubens. (A. 709.) *Venus Frigida.*
1615. *Rubens. (A. 312.) *Our Lady with the Parrot.*
1620. *Jacob Jordaens. (A. 844.) *Meleager and Atalanta.*
1630. *Van Dyck. (A. 403.) *Descent from the Cross.*

1640. *Hecken. (R. 1119.) *The Butcher's Shop.*
1654. Jan Victors. (R. 2553a.) *The Grocer's Shop "de Buyskool."*
1658. Bega. (M. 400.) *Tavern Scene.*
1665. Hanneman. (G.) *Portrait of Elizabeth van Limborgh.*
1671. Vaillant. (R. 2341.) *Portrait of Maria van Oosterwyck.*
1800. *Taco Scheltema. (G.) *Portrait of a Man.*

¶ Red Lead or Minium

The red-to-orange coloured Pb_3O_4 is obtained by simply heating, to not too high a temperature, white lead or lead oxide in contact with oxygen (air). The employment of this pigment is therefore closely connected with the use of white lead. The most suitable temperature for the transformation lies between 425° and 450°, as has been determined by Brown and Nees.[1]

A number of specimens of red lead were investigated by them microscopically, as a result of which some of the specimens showed a recognisable crystalline form, whilst others were completely amorphous.

Red lead possesses a great covering-power as a pigment, but it is less suitable as an artist's paint, since a brown coloration readily occurs on account of the formation of a little PbO_2.

This suggests the action of an acid, for example:

$$\underset{\text{(red)}}{Pb_3O_4} + 4HNO_3 = 2Pb(NO_3)_2 + \underset{\text{(brown)}}{PbO_2} + 2H_2O.$$

This reaction even occurs with dilute acetic acid after moderate heating. It is therefore not impossible that this reaction takes place to a slight extent when the pigment is subjected to atmospheric action.

[1] *Journal of Industrial and Engineering Chemistry*, 1912, part iv. p. 867.

Use can be made in microchemical analysis of the colour-change which occurs through the action of nitric acid. The transformation into brown PbO_2 can be clearly observed, especially by reflected light. After evaporating to dryness one can take up the residue in acetic acid and detect lead by means of the triple nitrite reaction (Plate 6). In addition, for the further confirmation of the PbO_2 in the nitric-acid solution, one may add a little oxalic acid, after which the liquid becomes quite clear.

No red lead was found in the specimens of red pigment investigated.

¶ Red Ochre

To the colour-series of the ochres belongs a variety with an iron oxide percentage and of a red-brown tint which closely approximates that of vermilion.

The appearance in the microscope differs little from that of the ochres generally. One will, however, generally come across only one kind of coloured particle, and not, as in the yellow and brown ochres, particles of various tints. Colourless particles also, which are generally doubly refractive, are in this case always present.

The recognition of the red ochre takes place in the same manner as with the other ochres, namely, by the detection of iron as Prussian blue.

Mention has already been made of the cases in which red ochre was present along with the yellow and brown ochres, as the difference between these and red ochre cannot be sharply defined.

¶ Organic Red Pigments

The most important colouring matter belonging to this group of pigments is of animal origin. It is obtained from the cochineal insect, which is to be found on various exotic cactus plants, the colour being known as carmine. When it is boiled out with water, to which alum has been added, and precipitated with a little soda, the red extract is precipitated on aluminium hydroxide and can be used after drying as a pigment.

As with most of the organic colouring matters, the colouring power is strongly developed, so that an intense colour is communicated to the oil even by a small quantity of the pigment. Consequently the amount of colouring matter in specimens of paint is extremely small—too small for any specific reaction to be carried out with certainty.[1]

The appearance in a microscope with 100 × magnification clearly shows the organic character of the substance by the complete absence of any grain, and it gives the impression that only a coloured layer of oil is present. In order to establish that character, one can also bleach it with an alkaline solution of chloride, which reaction can be carried out with all organic red colouring matters.

Besides carmine, madder lake must also have been used formerly as a pigment. This latter is the product of the madder root, which was of Dutch origin.

[1] For details about the exact chemical composition of carmine and madder see Perkin and Everest, *The Natural Organic Colouring Matters*, 1918, pp. 95, 23.

The organic red pigments have a very small covering-power, and are consequently employed only in mixtures or as glazing paints. Beautiful effects can be obtained especially when they are glazed over an under-painting of vermilion; but they can also be glazed, for example, over a blue under-painting, whereby violet colours are produced.

Their permanence under the action of light appears to be generally very good, the oil obviously exercising a protective influence. Sometimes, however, signs of fading are perceptible, when the colour is still well preserved in the rabbet of the frame while it is much paler on that part of the painting which is exposed to light. The unusual pale colour which occurs on the painting of the faces of many portraits by Terborch must probably also be attributed to the fading of the red.

Organic red pigments were encountered in the 18 *specimens of paint mentioned in the following list. It appears that their use was already very general in the* 16*th and* 17*th centuries.*

1450. *Rogier van der Weyden. (A. 393.) *The Bloodless Offering of the New Covenant, symbol of the Bloody Offering of Golgotha.*

1490. *Hans Memling. (A. 780.) *Angels playing various instruments.*

1500. *Benson. (A. 262.) *The "Deipara Virgo" announced by Prophets and Sibyls.*

1515. Jacob Cornelisz van Oostzanen. (A. 523.) *The Virgin Mary and the Christ-Child.*

1515. *Jan Provost. (A. 838.) *The Martyrdom of Saint Catherine.*

1540. *School Engebrechtsz. (A. 532.) *Before the Crucifixion.*

1600. *Wyttewaal. (M. 223.) *Mars and Venus.*

1600. *Pieter Breughel, the Elder. (Copy, A. 776.) *The Census at Bethlehem.*

1600. *Jan van Eyck. (Copy, A. 415.) *The Holy Pilgrims.*

1614. Rubens. (A. 709.) *Venus Frigida.*
1615. *Rubens. (A. 312.) *Our Lady with the Parrot.*
1616. Frans Hals. (F.H. 123.) *Banquet of Officers of the Civic Guard of St. George.*
1627. Frans Hals. (F.H. 125.) *Banquet of Officers of the Civic Guard of St. Adrian.*
1640. *Hecken. (R. 1119.) *The Butcher's Shop.*
1641. Frans Hals. (F.H. 128.) *Guardians of the St. Elizabeth Hospital.*
1710. *Van Huysum. (M. 70.) *Flowerpiece.*
1710. *Van Huysum. (M. 71.) *Flowerpiece.*

CHAPTER VI

GREEN PIGMENTS

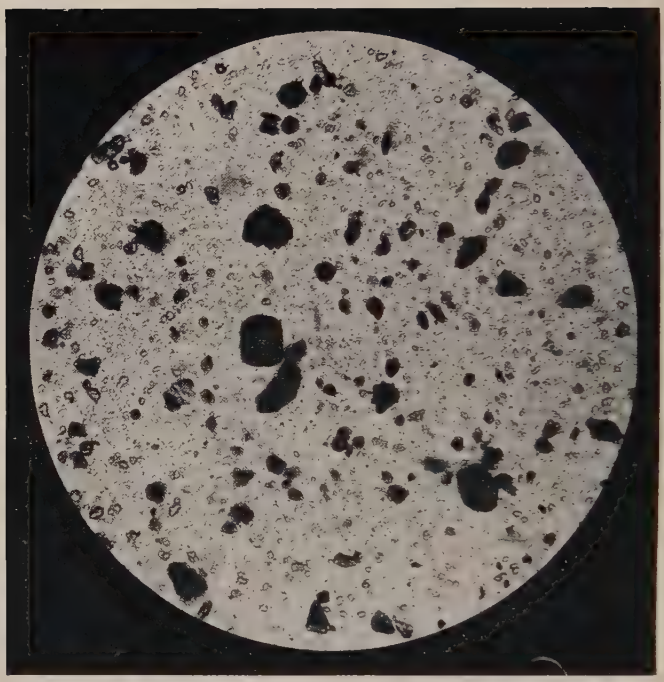
¶ Terre Verte

This pigment, although not possessing an intense green colour, appears to have been universally used by the old masters, probably because it was easy to obtain and consequently cheap. It must be classed with the ochres, and, as far as its composition is concerned, it agrees closely with them.

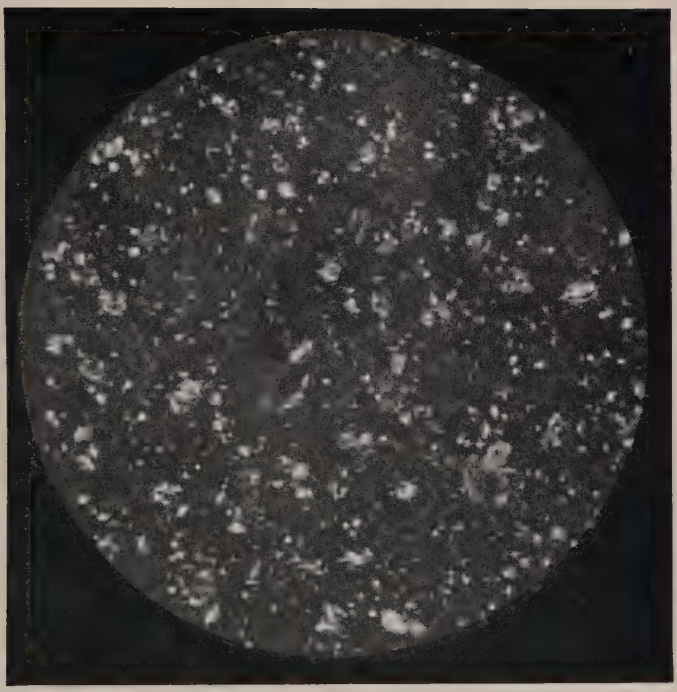
Microscopically considered (Plate 26), it immediately gives the impression of a product with a very heterogeneous composition, and one supposes at first that one is dealing with a mixture of an ochre with some blue pigment or other. Besides all the characteristic constituents of an ochre, there are clearly visible strongly coloured blue particles which have the external appearance of cobalt blue, and of which the refractive index is also greater than that of nitrobenzene, as is the case with cobalt blue. The test for cobalt has, however, a negative result; and a difference, which is very striking, is that the blue particles are doubly refractive, which is not the case with cobalt blue (Plate 27).

Besides the microscopical examination, the indication of the presence of iron is the main point to be dealt with: this can be done by igniting several times with strong sulphuric acid (in which all organic matter disappears at the same time) and subsequently confirming as Prussian blue.

Terre verte has small covering-power, although this may vary with the differently coloured varieties. Paintings which have been made with the unmixed



26. TERRE VERTE (105×)



27. TERRE VERTE (105×)

The same specimen between crossed nicols

28. VERDIGRIS (210×)

pigment have often a characteristic granular surface in the unvarnished condition which also occurs with smalt; and this variety of ochre is sometimes also subject to some weathering, a phenomenon which can be observed on paintings where greyish patches appear in the green.

The pigment appears to have been used principally in the 17th century and less in the 18th century, because one could then obtain various shades of green by using Prussian blue and mixing with yellow pigments, although they are not identical with the green of terre verte. Even at the present time the pigment is still in use to a small extent.

Terre verte could be detected in the four specimens of paint mentioned below.

1630. *Salomon van Ruysdael. (M. 566.) *The Bridge.*
1640. *Lapp. (M. 84.) *Italian Landscape.*
1654. Jan Victors. (R. 2553a.) *The Grocer's Shop "de Buyskool."*
1840. *B. J. van Hoven. (G.) *The Heerengracht at the Hague.*

¶ Green Pigments containing Copper

The group of green pigments containing copper can be divided into three parts, each of which represents a definite type.

1. Basic copper carbonates. The natural product which belongs to this class is malachite. In addition there also exist artificially prepared basic carbonates, which, however, are used but little or not at all, because their colour does not supply a definite want and their stability is not always great when they are employed as oil-paints.

2. Basic copper acetates, which have been known from antiquity as Verdigris.
3. Copper compounds which also contain arsenic. Of these Scheele's green and emerald green are the most important. A very large number of products, particularly of this last group, are on the market under the most diverse names.[1]

¶ Malachite

Except for the colour, the external appearance and the properties of this pigment are almost wholly analogous to those of azurite, which often occurs together with it in Nature. Consequently there is a high refractive index and double refraction, while, in contra-distinction to azurite, malachite dissolves with effervescence in warmed acetic acid. The composition of malachite corresponds to $CuCO_3 . Cu(OH)_2$.

After one has observed the effervescence with acids, one can evaporate, take up in acetic acid and detect the copper by means of the triple nitrite reaction (Plate 6).

It appears from the following list of 6 *specimens of malachite that this pigment was used in the main by the painters of the Flemish school.*

1500. *Quinten Metsijs. (A. 29.) *Saint Christopher.*
1500. *Hieronymus Bosch. (A. 840.) *Our Saviour mocked by the Soldiers.*
1530. *Jan Swart. (A. 207.) *The Adoration of the Kings.*
1600. *Jan van Eyck. (Copy, A. 415.) *The Holy Pilgrims.*
1600. *Pieter Breughel, the Elder. (Copy, A. 776.) *The Census at Bethlehem.*
1610. *Pieter Breughel, the Elder. (Copy, A. 777.) *The Sermon on the Mount.*

[1] In this connection see, for example, Eibner, *Malmaterialienkunde*, Berlin, 1909, p. 174.

¶ Verdigris

There is a general agreement between the old recipes[1] for the preparation of this pigment. One starts with copper turnings or filings and puts these together

[1] *Secreet-Boeck*, 1609, p. 218 *et seq.*

"Hoe datmen Spaensgroen maken sal.

"Neempt coperbladers | en vijlsel van coper | doet die in een dicke coperen Busse | met een decksel daertoe eygetlic gemaeckt wesende: Giet daer op goeden stercken Wijnazijn | ende een weynich honich settet inde warme Sonne | oft op eened warmen hoven | veertyien dagen lanc | so sal den Azijn daer van Blauverwich worden | giet die daer af | in een galas stopt dat dichte toe | en giet wederom Azijn | en honich daer af latet wederom so lange staen | gietet wederom af | en doet dit soolanghe als het Coper Verwe van hem geeft. Het gee dater afgegoten is | dat suldy laten staen | tot datet begint dicke te worden. . . ."

"How to make Spanish Green (=verdigris).

"Take copper sheet and copper filings and put them into a thick copper vessel with a well-fitting lid. Pour good strong vinegar on them and also a little honey, and put it in the sun or on a warm oven for fourteen days. Then the vinegar will have become blue; pour this off into a glass and close tight. Then pour in vinegar and honey again, and let it stand once more; pour off again as long as the copper produces paint. Let that which you have poured off stand until it begins to thicken.")

("Grieckxgroen, ofte Spaensgroen.

"Neempt Coperplaten | bestrijctse | met geschuymden honich hanctse in eenen verloyden Pot | boven dichte toegedect | giet stercken Azijn | inden gront | stelt dezen Pot also | op een warme plaetse vyer ofte vijf weken lanc | doet daer naer den Pot ope | en schrabt de griene blomme van de Coperplate. Hanct de plate wederom daer in als vore | en doet ooc altijt de groene blomme daer van | so lange als de plate duyrt. . . ."

("Greek Green or Spanish Green (=verdigris).

"Take copper sheet and smear it with skimmed honey and then hang it in a glazed pot which is closed tight at the top. Pour strong vinegar on it and bury it in the ground in a warm place for four or five weeks. Afterwards open the pot and scrape the green off the copper sheet. Then hang the plate in again as before and scrape the green from it, continuing as long as the plate lasts.")

with acetic acid, vine tendrils or pressed grapes. If moderate heat is then applied, the copper is attacked in course of time and a basic acetate is formed. The mass can be lixiviated and the product recrystallised from acetic acid, after which it can be used as a pigment.

The crystals have the form of pointed needles when they are observed through the microscope. They are often united into bundles, while the larger pieces show a fibrous structure (Plate 28). If, however, the pigment is not recrystallised but ground directly, then it is seen as transparent grains. A strong double refraction can be observed and the refractive index is below that of nitrobenzene ($n = 1{\cdot}55$).

The basic acetate dissolves extraordinarily easily in dilute acetic acid, in which the copper can then be detected by the triple nitrite reaction (Plate 6). If one has a sufficient quantity of a dry specimen, by distillation with a little concentrated sulphuric acid acetic acid can be obtained, which can then be confirmed by conversion into sodium uranyl acetate.

The pigment in oil is in a very fine state of division, and a specimen of paint will as a rule contain only a small quantity of pigment, since it is used mainly as a glazing paint. Sometimes, when it is mixed with oil, a little copper soap, which is also very finely divided, is also formed because of the presence of free fatty acids in the oil.

From the list given below of 9 *specimens of paint, it appears that verdigris was mainly used by the painters of the Flemish school.*

1510. *Master of Antwerp. (A. 385.) *Jesus in the midst of the Scribes.*

1525. Barend van Orley. (A. 741.) *The Last Judgment and the Seventh Work.*
1530. *Bruges Master. (A. 535.) *The Holy Virgin.*
1540. *School Engebrechtsz. (A. 532.) *Before the Crucifixion.*
1550. *Marinus van Reymerswael. (A. 244.) *The Tax-gatherers.*
1600. *Wyttewaal. (M. 223.) *Mars and Venus.*
1601. Marten de Vos. (A. 83.) *The Tribute to Caesar.*
1614. Rubens. (A. 709.) *Venus Frigida.*
1620. *Rubens. (Copy, A. 315.) *The Descent from the Cross.*

¶ Scheele's Green

The researches which Scheele carried out on arsenic led in 1778 to the discovery of this pigment,[1] which consists of copper arsenite, $Cu(AsO_2)_2$.

It was prepared by adding together solutions of copper sulphate and potassium arsenite. The latter solution was obtained from arsenic trioxide and potassium carbonate, and probably always contained a small excess of carbonate. Since Scheele's green always contains a little basic copper carbonate, the colour may vary somewhat in proportion to the amount present.

Microscopically considered, the pigment consists of small and large green flakes which are only slightly transparent, without any regularity of shape which can be recognised. The refractive index is above that of nitrobenzene but below that of methylene iodide. The pigment dissolves in nitric acid if gently warmed; and after evaporation and taking up in acetic acid, copper can be detected by the triple nitrite reaction (Plate 6).

The presence of arsenic can be confirmed by treating with zinc dust and hydrochloric acid.

[1] Kopp, *Geschichte der Chemie*, Berlin, 1847, part 4, p. 196.

The covering-power of this pigment is fairly large; its highly poisonous nature has, however, stood in the way of its use on a large scale, and it has now passed completely into disuse through the universal employment of emerald green.

No Scheele's green was encountered in the specimens of green paint investigated.

¶ Emerald Green

At the beginning of the 19th century the manufacture of Scheele's green led to the preparation of a copper arsenite which contained, in addition, copper acetate in the ratio of three molecules of $Cu(AsO_2)_2$ to one molecule of $Cu(CH_3COO)_2$.

This new pigment was prepared for the first time in 1814 by Rusz and Sattler[1] in Schweinfurt, and the manufacture soon grew to such an extent that the product was even named after the place where it was prepared. The colour of the compound is intense green.

Copper and arsenic can in this case also be detected in the same way as with Scheele's green. With small quantities there thus exists no chemical reaction which can satisfactorily distinguish between them.

The shape of the grains is, however, a certain means of making this distinction. Emerald green consists practically exclusively of round grains of almost equal dimensions. The radial structure of the grains is specially characteristic of this pigment, which structure can be very clearly recognised with high

[1] Rose, *Die Mineralfarben*, Leipzig, 1916, p. 140.

29. EMERALD GREEN (210×)

30. ZINC GREEN (210×)

magnification (Plate 29). The refractive index in this case also is above that of nitrobenzene but below that of methylene iodide, but there is also a strong double refraction, in contrast with Scheele's green.

The pigment is quite suitable for an oil-paint and is fairly stable. Mixture with pigments containing sulphur (for example, cadmium yellows) must, however, be avoided and precautions must be taken against its poisonous nature.

Emerald green was met with in a painting dating from about 1860.

1860. *L. J. Kleyn. (G.) *A View of the Hague.*

¶ Zinc Green

This pigment was first prepared by the Swede Sven Rinman in 1780[1] by heating the precipitate which he obtained by precipitating a solution of zinc nitrate and cobalt nitrate with caustic soda. It was only at about the middle of the 19th century, when zinc white was manufactured in large quantities, that there was any question of a practical application of Rinman's discovery.

Zinc green is obtained by moistening zinc white with a solution of a cobalt salt and then igniting the mass. The green product varies but little in colour when the amount of cobalt salt is varied, which gives rise to the conjecture that the colour must be attributed to a compound of invariable composition. The investigations of Hedvall[2] have, however, made it probable that we have to do in this case, as

[1] *Berichte der Deutschen Chemischen Gesellschaft*, 1912, vol. 45, p. 2095. *Zeitschrift für anorganische Chemie*, 1914, vol. 86, p. 212.

[2] *Ibid.*

distinct from cobalt blue, not with a definite compound but with solid solutions of the two components.

The formation of the green product takes place even at red heat, but more quickly at higher temperatures. The pigment covers well, is very stable and may readily be employed in mixtures.

When it is viewed under the microscope, round transparent grains (Plate 30) are visible, and these have a refractive index above that of methylene iodide.

Solution takes place very easily in nitric acid; and after evaporation and taking up in acetic acid, zinc and cobalt can be tested for together by adding ammonium-mercuric-thiocyanate. The crystals have the shape of the corresponding zinc compound on account of the great excess of zinc, but are coloured light blue by the presence of cobalt (Plate 17). With larger quantities the cobalt can be confirmed by means of the borax bead test.

No zinc green was found in the specimens of green pigments which were investigated.

CHAPTER VII

THE RESTORATION AND PRESERVATION OF PAINTINGS

The preservation of materials or objects is generally intended to ensure their continuing in the state in which they now exist. This, however, is not enough when it is a question of preserving a picture. Then an attempt has usually to be made to restore it to a previously existing state which agrees entirely, or as nearly as possible, with its state at the time of the original production. The preservation must therefore be accompanied by a restoration, which must include the whole picture. Both the painting and the varnish-layer, which are closely connected with one another, have to be improved in restoration.

There has been, in the course of time, no lack of attempts to improve the appearance of paintings,[1] but the first systematic investigations in this province date from the second half of the 19th century, when a general appreciation of the old masters came into prominence and the necessity of getting their productions into a good state and of preserving them for later ages was recognised.

The oldest known investigations concerning the restoration of paintings were carried out by Max von Pettenkofer, and led to his at first patented regenerative method.[2]

A layer of varnish, which generally consists of

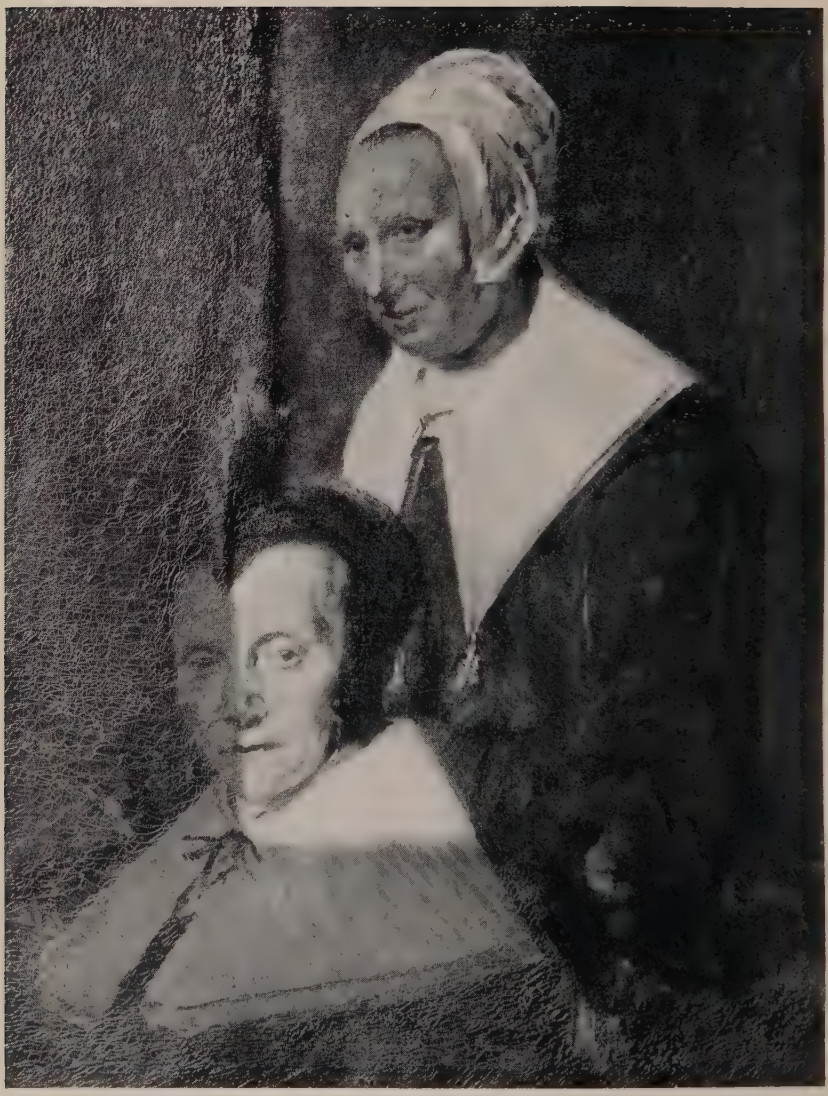
[1] In this connection see, for example, Morits Stübel, "Gemälderestaurationen im 18. Jahrhundert," *Der Cicerone*, 1926, vol. xviii. p. 122.

[2] *Über Ölfarbe und Conservirung der Gemälde-Galerien durch das Regenerationsverfahren*, Braunschweig, 1870.

a thin layer of mastic, becomes in the course of time tarnished, dull and opaque, turns yellow, and is filled with a network of fine cracks, as a result of which the coherence of the layer is entirely lost. Not only is the optical effect of the colours seriously spoiled on this account, but at the same time, as a consequence of its great penetrability, there can no longer be any question of a protective action of the varnish. The coherence is quite disturbed even by rubbing lightly on the varnish-layer, and the painting becomes covered with a layer of powdered resin. By continued rubbing, in which the powdered resin serves further as a grinding material of the same hardness as the original varnish-layer, it is for the most part possible to remove it from the painting by this dry method.

The regenerative process has the object of rendering once more transparent the residual portion of the varnish-layer, which is now very dull and opaque, and of uniting it to a coherent layer. It can be carried out in the following manner:—By placing on the painting a wooden box padded on the inside, the padding being moistened with a little alcohol, one subjects the resin-layer to alcohol vapour. After a certain time, depending on the thickness of the layer and the nature of the resin, the box is removed and on the place on which the alcohol vapour has acted a transparent, glossy varnish-layer is once more to be seen. When the whole surface of the picture is treated successively bit by bit in this way, the old varnish-layer becomes regenerated.

The explanation of the process, which takes place entirely at room temperature, is as follows:—The space under the box is completely saturated with



31. FRAGMENT OF "THE LADY GUARDIANS OF THE ALMSHOUSES FOR OLD MEN" BY FRANS HALS (1664), IN THE FRANS HALS MUSEUM AT HAARLEM

From a part the old yellow varnish has been removed

32. FRAGMENT OF "THE LADY GUARDIANS OF THE ALMSHOUSES FOR OLD MEN" BY FRANS HALS (1664), IN THE FRANS HALS MUSEUM AT HAARLEM

From a part the old yellow varnish has been removed

alcohol vapour. Since the resin is soluble in alcohol and the vapour pressure of the solution is lower than that of the pure alcohol, the alcohol vapour and the resin together form a concentrated alcoholic solution of resin. A clear solution of resin is thus produced in the painting, and when the box is removed the alcohol will evaporate into the air and the resin will remain behind as a coherent transparent layer.

Pettenkofer always speaks in his book of a "swelling" of the varnish-layer, which explanation is still given also by Doerner.[1] It is clear that this purely physical process only brings about an alteration of the form in which the resin layer was present on the picture. The material properties of the resin are not changed by it, and consequently the varnish-layer will after some time again pass into the state which existed before the treatment. Pettenkofer also realised this, and attempted to remedy this defect by improving the old varnish-layer during or after the treatment by the addition of copaiva-balsam. This led to the use of copaiva-balsam as a varnish for paintings. There are, however, several objections to this: for example, the varnish turns yellow within a rather short time.[2]

The regenerative process aroused much interest at its first introduction, a clear idea of which is given by Mulder's description.[3] Regeneration by Pettenkofer's method can give very good results for a time, but they are not of a permanent kind, especially when copaiva-balsam has been used. As mentioned before,

[1] *Malmaterial und seine Verwendung im Bilde*, München, 1922, p. 344.

[2] In this connection see C. F. L. de Wild, *Bulletin van den Ned. Oudheidk Bond.* 1909, 2nd series, vol. 2, No. 2.

[3] *Scheikundige verhandelingen en onderzoekingen*, part 4. *De scheikunde der droogende oliëen en hare toepassing*, Rotterdam, 1865, p. 324 *et seq.*

the latter is fairly quickly subject to an alteration of colour: it becomes yellow and thereby alters the whole appearance of the underlying painting through unnatural colour relations. The yellow varnish screen has a peculiar influence; while reds are the least affected, blues become brown, yellows darken and the whites assume the exact colour of the varnish. Furthermore, the copaiva-balsam is but little resistant to the variable influence of the water vapour from the atmosphere, and cracks from this cause after a relatively short time. The varnish-layer can then again be treated in the same way—with, however, always the same temporary result. Finally the layer becomes so thick and consists of layers of such different ages that it is no longer possible to regenerate it adequately.

To produce a permanent improvement of the varnish-layer, the only way is to remove it completely and replace it by a new one. The varnish-layer of the painting can be removed by means of a suitable solvent, for which purpose alcohol is especially indicated. One can interrupt the action of the alcohol by means of turpentine at the moment when the painting is reached.

The paint-layer is very resistant to the action of turpentine and also to that of alcohol, provided that care is taken that the contact with the paint is not of too long a duration.

The dried binding-medium of the paint-layer, the linoxyn, has the property of swelling to a greater or less extent in organic liquids.[1] If this is noticeably

[1] For the phenomena which appear with swelling, see, among others, Katz, *Die Gesetze der Quellung*, *Kolloidchemische Beihefte*, 1917, vol. ix. Nos. 1-6.

the case, the paint-layer becomes soft and a danger exists of a mechanical removal. It is unnecessary to state that this must be prevented, above all. If one allows the solution of the resin-varnish to take place quickly, then with a suitable treatment there is no danger whatever that the paint-layer (at any rate of old paintings) will be attacked. When the action of the alcohol is too rapid to be adequately controlled, *e.g.* with paintings of more recent date, the action can be delayed by the addition of an inactive volatile liquid—for example, xylol.

The property of swelling is practically no longer present in old, completely hardened paint-layers; with thin glazings, however, nothing can be determined with certainty beforehand.

By the removal of the coloured and cracked varnish-layers, it is thus possible to bring the appearance of a painting back to what it was at the time of its production (see Plates 31, 32 and 33), at least if we neglect the alterations which have appeared in the course of time in the paint-layer. These are of two kinds—changes in colour and changes in coherence. The pigments, which have already been discussed in the preceding pages, have, with a few exceptions, retained their original colours, and the discoloration of the binding-medium is only of significance with paints containing much oil.

The alterations in the coherence of the paint-layer are usually much more drastic. With paintings which have been made on a primed canvas, the priming and the paint-layer in normal cases form an inseparable whole after the binding-medium has dried. The foundation—the canvas, which is stretched tightly on a wooden frame—is continually subject to altera-

tions of tension through the influence of the variable humidity of the atmosphere. The foundation is thus a surface which is continuously in motion and the paint-layer is compelled to take part in these movements. This can take place without difficulty with a new paint-layer; when, however, the layer becomes older and consequently the hardness increases and the elasticity decreases, then the movement of the foundation leads to the appearance of a characteristic formation of cracks—the crackle or *craquelure*. The ruptured paint-layer, however, still remains firmly attached to the canvas. At a later stage the edges of the cracks begin to rise and come loose from the canvas. The painting, through this cause, becomes very susceptible to atmospheric influences, and the coherence between the canvas and the paint becomes continuously less. Finally portions of the paint-layer fall off. When at the same time the strength of the canvas has declined, then the painting has arrived at such a state that a complete falling-off of the paint-layer within a relatively short time has to be reckoned with. In order to bring about an improvement in, or apply a remedy for, this condition, it is necessary to reline the painting. The most satisfactory way in which this can be done is the wax-process.

A new piece of canvas is placed behind the old canvas, whilst the picture is supported on the front face by means of a paper covering. The attachment of the new to the old canvas is obtained by applying molten beeswax to the back of the new canvas, and by making this wax flow through the new canvas, the old canvas and all the cracks and openings in the paint-layer by means of heated irons. Then, after

Photo, Vinkenbos & Dewald, The Hague

33. "THE LADY GUARDIANS OF THE ALMSHOUSES FOR OLD MEN" BY FRANS HALS (1664) IN THE FRANS HALS MUSEUM AT HAARLEM

Present condition after entire removal of the old yellow varnish

34. PAPER COVERING FROM A PICTURE RELINED AFTER THE WAX-PROCESS ON WHICH THE CRACKLE HAS BEEN DEPICTED BY THE WAX

having penetrated the whole picture, the wax imprints itself on the paper covering (see Plate 34). When this stage has been reached, one is certain that the whole picture, in all its pores and openings, is completely filled with wax. After this has cooled, the paper covering is taken away and the surplus wax is removed from the front of the painting by means of a solvent.

Pictures which have been relined, as it is called, with glue—that is, when a new canvas has been stuck behind the old one by means of glue—compare unfavourably with those which have been treated by means of the process described above.

From a comparative study of fabrics which had been soaked in glue, in adhesives containing glue and in wax respectively, carried out in the laboratory of physical chemistry at the Technical University of Delft, I found that the fabric soaked in wax retained a constant weight while subject to a variable degree of humidity, whilst those soaked in glue absorbed water perceptibly, in quantities which increased with the degree of humidity. This phenomenon further appeared to be reversible. At the same time, the glue process brings with it the danger that the picture may be scorched through the glue's requiring too high a temperature in order to do its work properly; and finally, there is no guarantee that sufficient penetration and filling up have taken place.

A movement of the foundation can similarly be observed with pictures which are made on wood (panel), although it is of much smaller extent than with paintings on canvas. The movements in this case mainly run perpendicularly to the direction of

the grain of the wood. If in the course of time a deformation (curvature) of the wood surface occurs, then it is necessary to apply a cradling to the back of the panel. In agreement with the greatest movement, which takes place perpendicularly to the direction of the grain, the cradling must be so applied that the laths which run parallel to the grain are rigidly fastened, while the laths which are placed perpendicular to the grain remain movable and the reversible alteration of shape through expansion and contraction is still possible. These points are illustrated in the cradling reproduced in Plate 35; the horizontal laths are thus movable, as is also visible. One may also point out the heavy vertical strip which is placed behind the glued joint of the panel in order to give it more support.

In discussing the methods of restoration and preservation, I have omitted the possibility that there may be over-paintings covering the original painting.

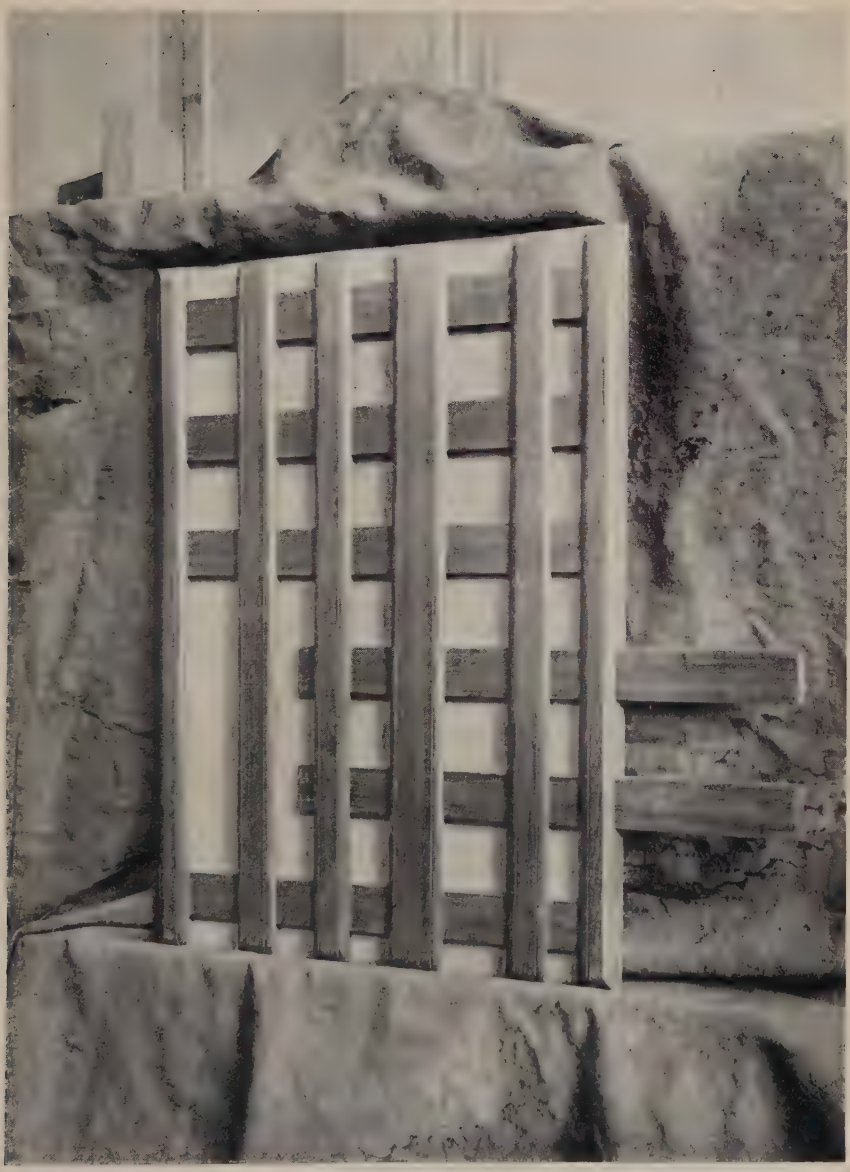
In this case two possibilities must be distinguished:

(1) That the over-painting is applied to the original without there being a varnish-layer in between them.

(2) That the two are separated by a layer of varnish.

In the first case it is for the most part very difficult or impossible to separate the over-painting and the original painting; indeed, it will never be found that an original painting differs much in age from an over-painting without the original having been varnished.

In the second and much more prevalent case, although the often relatively old over-painting



35. CRADLING APPLIED TO THE BACK OF A PANEL

Two of the horizontal laths are displaced to show the moveability

Photo, Vinkenbos & Dewald, The Hague

36. "BANQUET OF OFFICERS OF THE CIVIC GUARD OF ST. GEORGE" BY FRANS HALS (1616) IN THE FRANS HALS MUSEUM AT HAARLEM

Condition before removal of the old yellow varnish

Photo, Vinkenbos & Dewald, The Hague

37. "BANQUET OF OFFICERS OF THE CIVIC GUARD OF ST. GEORGE" BY FRANS HALS (1616) IN THE FRANS HALS MUSEUM AT HAARLEM

Present condition after entire removal of the old yellow varnish
The over-painted drapery in the left top corner is again visible

itself resists the action of a solvent, it is nevertheless sometimes removed through the solvent penetrating between the two layers and dissolving the resin which is in between them. That this at any rate sometimes occurs must be attributed to the fact that an over-painting is usually thin, and on that account is easily penetrable by a solvent. If at the same time it is much cracked, then it will be still more easily attacked.

In this lies the explanation why old paint can actually be removed sometimes by treatment with alcohol. An example of this, among others, is to be found in the drapery in the left-hand top corner of the painting by Frans Hals (F.H. 123), *Banquet of Officers of the Civic Guard of St. George*, which at an earlier time was completely over-painted, as a result of which the folds now visible were entirely hidden (see Plates 36 and 37).

The general opinion that old paint resists the attack of alcohol is thus often not correct without reservation.

CHAPTER VIII

X-RAY PHOTOGRAPHY OF PAINTINGS

The X-ray image obtained from a picture can serve the purpose of giving a direction to one's studies of its material construction.

The ground (canvas or panel), the priming-layer and the paint-layer, which show different absorption for X-rays, are reproduced in the photographic image each in its characteristic manner, and each can be accurately investigated as to its relation to the others.

As far as the absorption of the principal part of the painting, the paint-layer, is concerned, it is possible to calculate a quantity which, for the various kinds of pigments, gives an idea of the extent of that absorption. This quantity is called the mass-absorption coefficient, and, for a definite wave-length of the X-rays, is a measure of the absorption for those rays. It is expressed as $\frac{\mu}{c}$, in which μ represents the so-called linear absorption coefficient and c the density. The linear absorption coefficient, and hence the mass-absorption coefficient, is a function of the wave-length of the X-rays.

The mass-absorption coefficient of a chemical compound or of a mixture, in which various elements will occur in variable percentages by weight, can be found by multiplying the value of this quantity (for the same wave-length) for each of the elements by the corresponding percentage by weight, then adding and dividing by 100.

In this manner the mass-absorption coefficient

for a pigment can be found when the composition is known. With a mass of paint the amount of oil present must also be known. The volume taken up by the oil in a mass of paint may be calculated when further details are available with regard to the distribution of the particles of paint.

When one presupposes that the particles of pigment in a mass of paint are arranged tetrahedrally, that they touch each other, and that they take the form of spheres of equal diameter, then one can calculate that

$$\frac{\text{Volume of oil}}{\text{Volume of pigment}} = \frac{3\sqrt{2} - \pi}{\pi} = \frac{0.35}{1}.$$

With the same assumptions, but with a cubic arrangement, the ratio is

$$\frac{\text{Volume of oil}}{\text{Volume of pigment}} = \frac{6 - \pi}{\pi} = \frac{0.91}{1}.$$

When, however, this ratio is determined experimentally for a mass of paint, it appears that both with machine-ground and with hand-ground paint even the cubic arrangement is not generally attained, so that a larger amount of oil is always present than in the above-mentioned theoretical type of structure. For this reason, the amount of oil given in the table below is taken from practical data;[1] in the last column are recorded some of my own observations referring to hand-ground paint.

[1] The figures are taken from
(P) Pettenkofer, *Über Ölfarbe*, Braunschweig, 1902, p. 11.
(M) Morrell and de Waele, *Rubber, Resins, Paints and Varnishes*, 1921, p. 118.
A mean value from various data is taken for the specific gravities.

Pigment.	Specific Gravity.	Percentage by Weight of Oil.	Vol. of Oil. / Volume of Pigment.	Hand-Ground.
White lead .	6·8	6 (M) 11 (P)	0·47 0·90	1·15
Zinc white .	5·3	15 (M)	1·01	1·63
Cobalt blue .	3·5	55 (P)	4·60	..
Ochre . .	3·0	45 (P) 70 (P)	2·64 7·53	..
Carbon .	1·8	53 (P)	2·18	..
Vermilion .	8·2	20 (P)	2·20	2·60
Linseed oil .	0·93	..	..	..

The mass-absorption coefficients of a number of elements for a wave-length of 0·708 Å. have been determined and are recorded in Landolt-Börnstein.[1] The values in the table have been calculated with the help of these data.

The missing values of $\frac{\mu}{c}$ for H, Si and Hg were found as follows: H was calculated from the formula

$$\frac{\mu}{c} = A\lambda^3 + B,$$

in which $A = 0{\cdot}28$ and $B = 0{\cdot}37$, which is valid between the wave-lengths λ of 0·24 and 0·98 Å.[2]

The value of $\frac{\mu}{c}$ for Si was calculated from the known values for P and Al (the neighbouring elements in the periodic system) by making use of the fact that the values of $\frac{\mu}{c}$ vary approximately as

[1] *Physikalisch-chemische Tabellen*, 5th edition, Berlin, 1923, part ii., p. 860, Wingardh.

[2] *Ibid.* 1st Supplementary volume, 1927, p. 388; see also p. 386.

the third power of the atomic numbers, and then taking the mean of the numbers so obtained.[1]

The value for Hg was found from those for Au and Pb by linear interpolation, which in this case appears to be more accurate than an application of the above-mentioned third-power law.

The composition, $CoO \cdot Al_2O_3$, was assumed for cobalt blue, although in the actual pigment this compound occurs together with variable amounts of Al_2O_3, as a result of which the value of $\frac{\mu}{c}$ is actually smaller for this pigment. This will also be the case with smalt.

For the composition of ochre, a mean is accepted, taken from data by Rose;[2] whilst for the composition of natural ultramarine, that of Brögger and Backström[3] was chosen. The quantitative composition of linseed oil was taken from Fahrion.[4]

MASS-ABSORPTION COEFFICIENT OF VARIOUS PAINTS FOR A WAVE-LENGTH OF 0·708 Å.

Pigment.	Composition.	μ/c of Elements.	μ/c of Pigment.	Weight per cent of Oil.	μ/c of Paint.
Gold . .	100 % Au	100·9	100·9	..	..
Massicot .	92·8 % Pb	101·7	94·5	..	..
PbO . .	7·2 % O	1·00			
White lead	80·1 % Pb	101·7	81·7	11	72·7
$2PbCO_3$.	3·1 % C	0·667			
$Pb(OH)_2$.	16·5 % O	1·00			
	0·3 % H	0·47			

[1] For further details in this connection see, for example, Bouwers, *Physica en techniek der Röntgenstralen*, Deventer, 1927; Glocker, *Materialprüfung mit Röntgenstrahlen*, Berlin, 1927.

[2] *Die Mineralfarben*, Leipzig, 1916, p. 219.

[3] *Zeitschrift für Krystallografie*, 1891, part 18, p. 209.

[4] *Die Chemie der trocknenden Öle*, Berlin, 1911, p. 120.

MASS-ABSORPTION COEFFICIENT OF VARIOUS PAINTS FOR A WAVE-LENGTH OF 0·708 Å.—*contd.*

Pigment.	Composition.	μ/ρ of Elements.	μ/ρ of Pigment.	Weight per cent of Oil	μ/ρ of Paint.
Vermilion . HgS . .	86·2 % Hg 13·8 % S	101·2 8·827	88·5	20	70·9
Zinc white ZnO . .	80·3 % Zn 19·7 % O	55·22 1·00	44·5	15	37·9
Malachite $CuCO_3$. $Cu(OH)_2$.	57·5 % Cu 5·4 % C 36·2 % O 0·9 % H	46·33 0·667 1·00 0·47	27·0	..	..
Azurite . $2CuCO_3$. $Cu(OH)_2$.	55·3 % Cu 7·0 % C 37·1 % O 0·6 % H	46·33 0·667 1·00 0·47	26·0	..	..
Cobalt blue $CoO . Al_2O_3$	33·3 % Co 36·2 % O 30·5 % Al	38·11 1·00 5·276	14·7	55	7 0
Smalt . $CoO . K_2O$ $3SiO_2$.	16·9 % Co 36·6 % O 22·4 % K 24·1 % Si	38·11 1·00 16·21 6·66	12·0	..	..
Whiting (Chalk) . $CaCO_3$.	40·0 % Ca 12·0 % C 48·0 % O	20·17 0·667 1·00	8·6	..	..
Ochre . 20 % Fe_2O_3 16 % Al_2O_3 54 % SiO_2 10 % H_2O	14·0 % Fe 8·5 % Al 25·2 % Si 51·2 % O 1·1 % H	36·93 5·276 6·66 1·00 0·47	7·8	45	4·6
Natural . Ultramarine	15·48 % Si 14·82 % Al 18·16 % Na 13·60 % S 37·94 % O	6·66 5·276 3·392 8·827 1·00	4·0	..	..
Carbon .	100 % C	0·667	0·7	53	0·7
Linseed oil	77·6 % C 11·3 % H 11·1 % O	0·667 0·47 1·00	0·7	..	..

A consideration of the table shows that the kinds of paint which contain elements of high atomic number (Pb, Hg) show a very much greater absorption for X-rays than those with elements of low atomic number. At the same time it appears that the influence of the oil present is small compared with that of the pigment.

The kinds of paint which contain heavy metals, such as Pb and Hg, will consequently, on account of their strong absorption for X-rays, give decided contrasts compared with those containing light elements; and the fact that both of them occupy a prominent place in the material construction of paintings is a fortunate circumstance for X-ray photography. The manifold use of white lead and massicot, especially in old paintings, is the reason why a striking resemblance to the original picture is often to be found in the direct X-ray photo.

During the production of the X-ray photograph the flat paint-layer is situated immediately on top of the photographic plate or film, which is protected from the light. Consequently the shadow image so obtained agrees completely in its dimensions with those of the picture, so that an accurate comparison of the photograph and the painting is possible. For this reason a clear indication, sometimes reaching certainty, can be directly obtained of the form of an under-painting not visible to the eye, which has been covered with a new layer of paint either by the artist himself or by someone else.

Conversely, it is sometimes possible to obtain an indication from the X-ray photograph of pigments employed which may or may not be visible to the eye. Such conclusions are, however, restricted to

those pigments which contain heavy metals in sufficient quantities; with the other pigments the differences between their absorptive powers is too small.

In general, a photograph produced with soft rays gives the finest shades on the photographic plate, and brings out to advantage all the details of the ground, the panel or the stretcher. Further, by the preparation of a series of photographs of the same object with different angles of incident radiation, characteristic anomalies in the stretcher or panel can be accurately determined.

Little can be said about the time of exposure which is necessary for the production of a photograph, because both the X-ray installations and the objects to be photographed may differ very considerably among themselves.

The height of the focus of the tube above the painting can be made the same throughout with a fixed installation, and, for example, 30 inches may be chosen, whereby the times of exposure for different pictures will differ less from each other, although a test exposure will in general always appear to be necessary in order to obtain a good result. When the pictures are larger than the surface of the plate or film, the time of exposure and the method of development of all the photographs which together make up the whole picture ought to be made accurately the same, for the sake of comparison.

Conclusions cannot be drawn from an X-ray photograph with equal success with all paintings; the material construction in some cases can actually be an impediment. Some general facts may, however, be stated both for paintings on canvas and for paintings on panel.

¶ Paintings on Canvas

When a canvas is prepared as a ground for a painting it is almost always invariably primed. The priming, which as a rule consists of chalk, ochre and white lead, or a mixture of these substances, fills up the spaces between the threads of the canvas so that a flat surface is obtained. When X-rays fall on this primed canvas, they will be absorbed in different degrees by the threads of the canvas and the spaces between them which are filled with priming. The threads of the canvas have a smaller absorptive power than the spaces between them, so that a strong contrast appears on the photographic plate. The canvas is then clearly visible owing to the spaces between the threads being strongly marked. When, for example, a painting is made on a thick priming-layer containing white-lead, this latter will so absorb the X-rays that the effect of the painting may be negligible in comparison. I found this to be the case, among others, with the picture by Frans Hals (F.H. 125), *Banquet of Officers of the Civic Guard of St. Adrian*, in which the absorption of the paint-layer is small compared with that of the white-lead priming. It was, however, my object in this investigation to trace any abnormalities there might be in the canvas, which, thanks to the priming-layer, were clearly to be seen. At the same time, it appeared that the new canvas applied to the back of the original one was quite invisible in the X-ray photograph. This is not surprising, since the new canvas naturally had no priming-layer and consequently could produce no contrasts or only extremely faint ones on the film.

¶ Paintings on Panel

In general, the finest X-ray pictures are obtained with paintings on panel. A thick priming-layer, which in the case of paintings on canvas may spoil the result of the X-ray photograph, is among the exceptions with panels, so that the various absorptions of the painting are clearly reproduced on the photographic plate or film. Since the priming only fills up the hollows of the grain, the structure of the panel is visible practically without exception. Glued joints, supports attached to the back, or cradling which may be there are similarly clearly reproduced on the X-ray photograph.

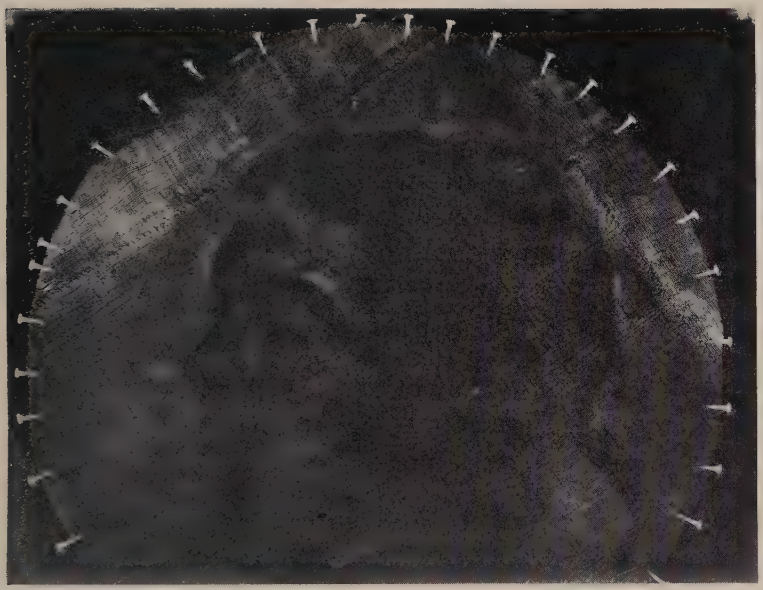
The very great advantage of investigation with the aid of X-rays lies in this, that, provided the object lends itself to the purpose, an absolutely certain indication is obtained of the whole material construction, without (and this is certainly of the greatest importance) the objects having to be the least bit injured.

In order to give an idea of the results which the X-ray photography of pictures can give, three practical cases will be described below. The illustrations belonging to the description correspond to the direct X-ray photograph.

A. The study by Rubens, *Head of a Girl* (Plate 38), diameter 34 cms., here reproduced after the removal of the varnish-layer, gave rise to the conjecture that there were some additions at the upper edge which were of recent date. In the X-ray photograph (Plate 39) one can see that to the old

Photo, Schwarz, Berlin

38. "HEAD OF A GIRL" BY RUBENS



39. "HEAD OF A GIRL" BY RUBENS

X-ray Photograph

canvas, which probably formed a fragment of a larger picture, two pieces of modern canvas have been sewed in order to give the whole a circular shape. These additions could not be noticed on the back of the picture, since it was relined at the same time.

The X-ray photograph at the same time clearly reproduces the structure of the original canvas, thanks to the priming-layer containing white lead, which fills up the spaces between the fibres. The priming-layer is not excessively thick, but it is the cause of the fact that the image of the painting has much less contrast than have the examples of paintings on panel which follow. The nails which fasten the canvas to the stretcher, on account of the fact that they do not lie in the plane of the painting but at some distance therefrom, are in the photograph displaced a little with respect to the circumference of the picture, through the rays' falling on them obliquely.

Nothing can be observed in the X-ray photograph of the canvas with which the painting was relined.

B. When examined the panel painting here reproduced (Plate 40), which is ascribed to Frans Hals and is to be found in the National Gallery of Scotland at Edinburgh (Catalogue No. 1200; size $18\frac{1}{4}$ in. × $13\frac{1}{2}$ in.), it appeared to me that there were traces of the brush strokes of hair under the red bonnet. An examination of the state of the paint with which the bonnet was painted showed that this must be of relatively recent date, judging by the very different properties which it showed compared with the under-paint-

ing. This fact together with the awkward, discrepant shape of the glass led to an X-ray examination. The photograph (Plate 41), which was prepared in the Royal Infirmary at Edinburgh with the kind assistance of Dr. Woodburn Morison, showed that the paint was in this case clearly indicated as a consequence of the thin priming-layer. Further, the structure of the panel is clearly visible through the priming over the whole surface. Of very remarkable interest also was the fact that the glass originally formed part of a long object, the nature of which could not be settled at first, but which stretched to the top of the head.

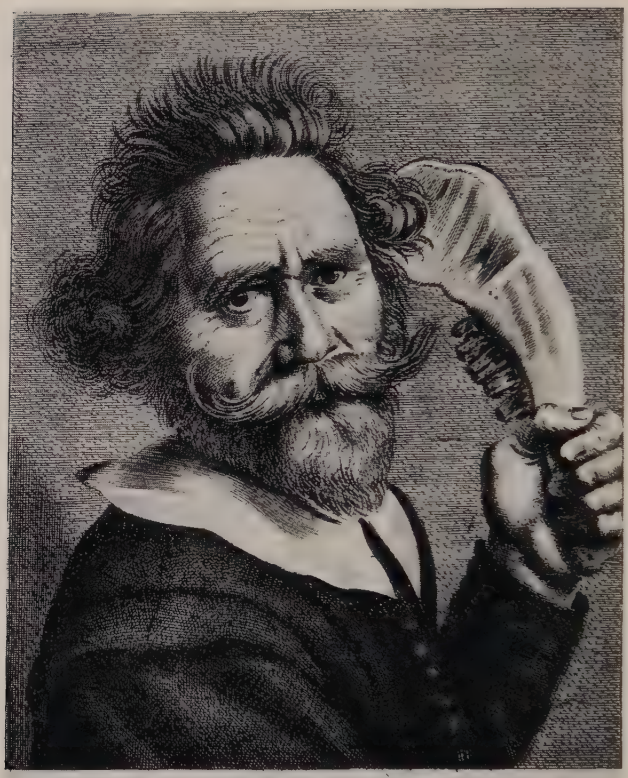
By this time it had thus been established that what is visible on this picture certainly did not constitute the original painting, but no correct idea of the true form of it could as yet be given. An important step further was the finding of the etching by Jan van de Velde (about 1568–1623) published by Bode and Binder (Plate 42). This represents the portrait of Verdonck, an intimate friend of Frans Hals, and is to be found in the Cabinet of Engravings at Amsterdam. According to Bode and Binder, it must have been made from a lost original painting by Frans Hals. From this information and also from the results of the scientific investigation which was carried out, I could now with the greatest probability conclude that the lost work of Frans Hals must be present in a sound condition underneath the over-painting. The fact that the priming-layer containing white lead, which shows up the structure of the wood over the whole painting, was absolutely intact would indicate that there had been no injury to the original painting underneath. Further, the brush strokes of

Photo, Annan, Glasgow

40. "THE TOPER" BY FRANS HALS, IN THE NATIONAL GALLERY OF SCOTLAND AT EDINBURGH

41 "THE TOPER" BY FRANS HALS

X-ray Photograph


Dit is Verdonck, die stoute gast.
Wiens kaekebeen elck een aen tast.
Op niemant, groot, noch kleyn, hy past.
Dies raeckte hy in t Werckhuis vast
Velde fecit.

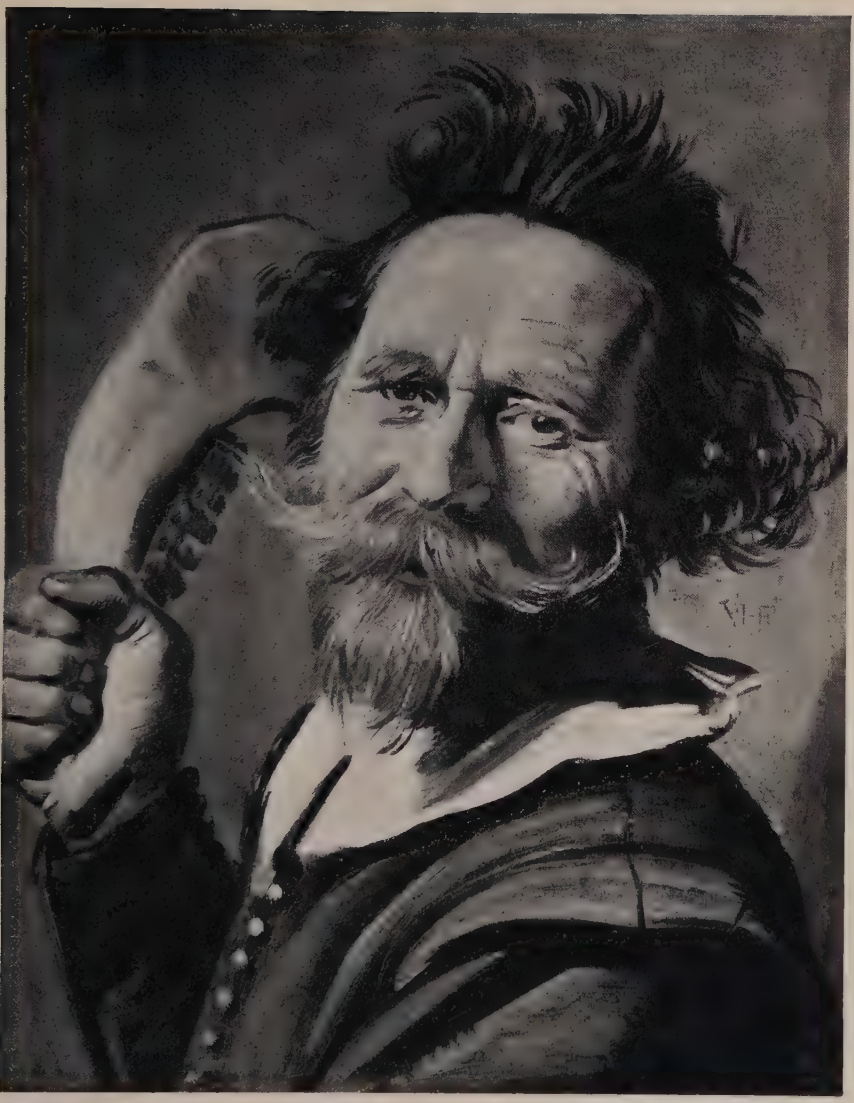
42. "THE TOPER," PROVING TO BE THE "PORTRAIT OF VERDONCK," BY FRANS HALS

Etching by Jan van de Velde

Photo, Dixon, London

43. "THE TOPER" BY FRANS HALS

Part of the over-painting has been removed



Photo, Annan, Glasgow

44. "THE TOPER," NOW THE "PORTRAIT OF VERDONCK," BY FRANS HALS, IN THE NATIONAL GALLERY OF SCOTLAND AT EDINBURGH

Present condition after entire removal of the over-painting

the hair under the red bonnet indicated that the under-painting still existed in a sound condition.

The Board of Trustees of the National Gallery of Scotland gave me the opportunity in the summer of 1928 of removing the over-paintings, and the reproductions given herewith (Plates 43 and 44) show that, thanks to the diagnosis made by purely scientific methods, the original work of Frans Hals was rediscovered.

C. My attention was directed by the Director of the Frans Hals Museum at Haarlem to a portrait of the Dutch school, representing Anna Dircksdr. van Bleyswijk (1603–1688) and painted on panel (F.H. 421; 70 × 59 cms.). Traces of a larger white cap are faintly visible in the background on the black head-dress (Plate 45). From this arose the suspicion that an over-painting had been applied at this place, and that also the rest of the costume had probably been partly altered. The four X-ray films, which were prepared in the St. Elizabeth's Hospital at Haarlem, form a whole which could be reproduced after transference to sensitive plates and printing on paper. The separations of the four original films are still faintly visible on the reproduction (Plate 46). It is unnecessary to describe the great surprise which these photographs produced; they speak for themselves.

A further investigation of nature of the pigments employed on this panel and the state of the paint-layer showed that the over-painting was very old and very probably dated from the 17th century. Whether the under-painting and over-painting can be separated will depend on the thickness of the latter

and the possible varnish-layer between the two, which cannot be determined without a closer investigation. The X-ray photograph in this case also shows the priming-layer containing white lead and the filling of the vertical joints of the panel.

¶ Examination of Paintings by Means of Ultra-violet Light

When the rays from a mercury-vapour lamp are passed through a dark-coloured quartz filter, the greater part of the visible rays are absorbed and the ultra-violet are separated from them. This principle is applied in the quartz analysing lamp, so that it is possible to expose various objects to the ultra-violet rays and in a dark room to investigate the phenomena occurring.

A large number of pigments have been examined under these circumstances by Eibner and others.[1] The results which were obtained by this investigation of coloured pigments appear, however, to be of relatively little value. Many of these pigments, which show very different colours in visible light, have in ultra-violet light a brown to black-brown tint, and consequently can hardly or not at all be distinguished from each other. By my own investigations these observations have been completely confirmed. In these it appeared how very difficult it is to describe the observed tints accurately, and that this description is to a high degree subjective. If one wishes to carry out an investigation by this method

[1] Eibner, Widenmayer and Stois, *Farben Zeitung*, 1923, part 31, p. 2399; Schmidinger, *Farben Zeitung*, 1923, part 31, p. 2451; Robl, *Zeitschrift für angewandte Chemie*, 1926, part 39, p. 609.

Photo, Vinkenbos & Dewald, The Hague

45. "PORTRAIT OF ANNA DIRCKSDR. VAN BLEYSWIJK," DUTCH SCHOOL, IN THE FRANS HALS MUSEUM AT HAARLEM

46. "PORTRAIT OF ANNA DIRCKDR. VAN BLEYSWIJK," DUTCH SCHOOL

X-ray Photograph

with any useful result, standard specimens will be indispensable.

White lead and zinc white display a striking difference when examined in ultra-violet light; the former appears to be practically pure white, while the latter shows a bright yellow colour. The difference still persists in spite of the fluorescence of the oil when the pigments are spread out as paint. The white lead, through the action of the binding medium, may sometimes take on a light violet colour. Consequently one has here a quick method of distinguishing between zinc white and white lead; to what degree the method can be used for mixtures of the two could be investigated in a further research.

When one examines paintings by ultra-violet light an influence makes itself felt which not only makes vaguer the small differences in tint between the coloured pigments, but also causes the difference between white lead and zinc white to be completely lost. This influence is the very strong fluorescence of the varnish-layer with which a painting is practically always covered. The effect of this is generally so predominant that the representation delineated in the picture is practically no longer visible. It is clear that this fact restricts the investigation with the quartz analysing lamp to exceptional cases.

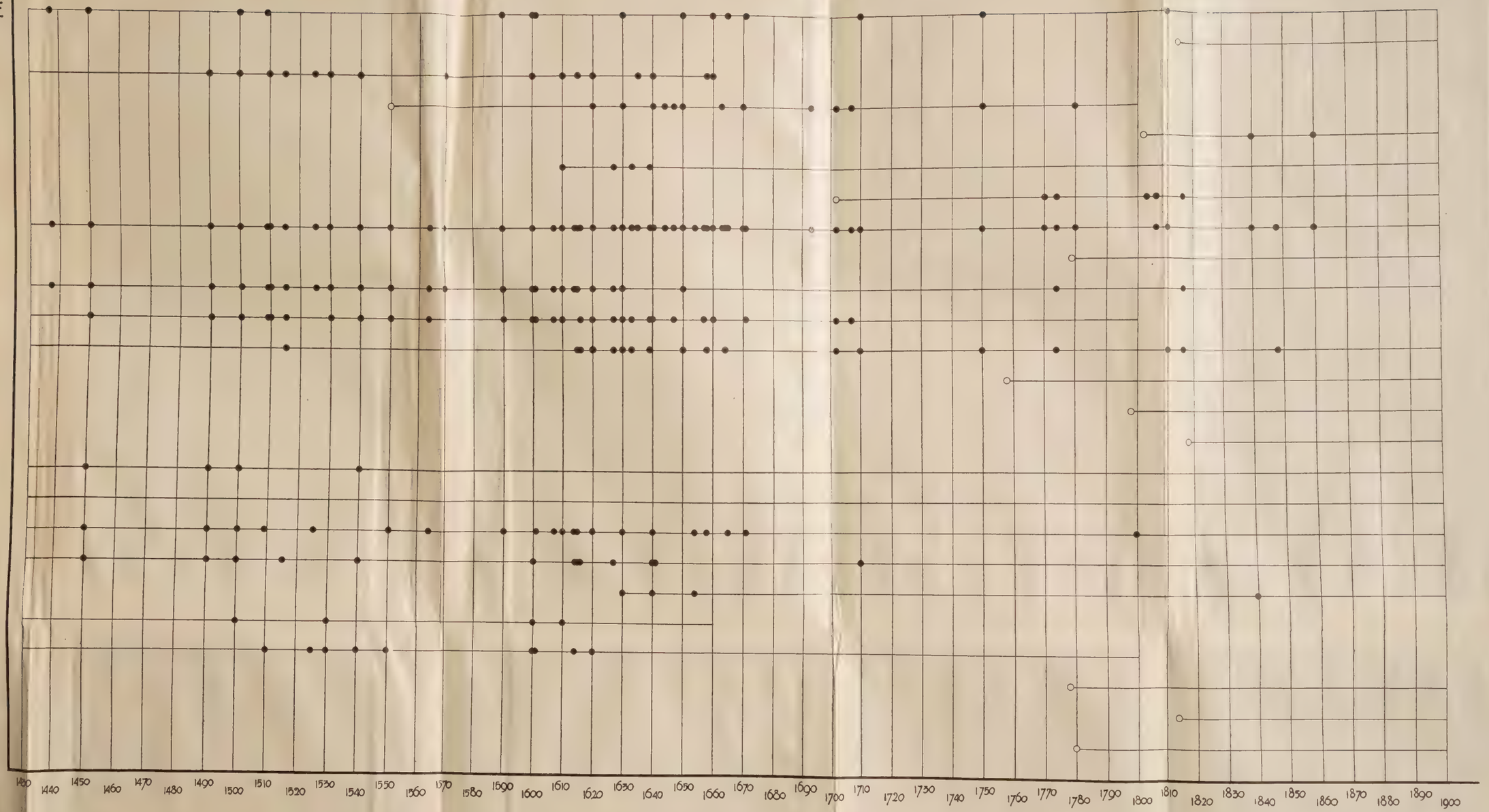
When a painting is entirely without a varnish-layer, then by an examination by ultra-violet light one can, for example, discover retouchings which do not consist of exactly the same pigments as the surrounding parts. Although these phenomena never give quite certain indications, they can show that a closer investigation is desirable. If a painting is covered with a layer of varnish, as has been men-

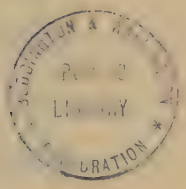
tioned above, conclusions concerning the underlying paint-layer cannot be obtained; it may, however, happen that one obtains indications of the existence of retouchings on the varnish-layer or of glazings of later date.

THE END

Chronological Chart of Pigments

- Natural Ultramarine
- Synthetic „
- Azurite
- Smalt
- Cobalt Blue
- Indigo
- Prussian Blue
- White Lead
- Zinc White
- Whiting
- Massicot
- Ochres
- Naples Yellow
- Chrome „
- Cadmium „
- Gold
- Carbon Black
- Vermilion
- Organic Red
- Terre Verte
- Malachite
- Verdigris
- Scheele's Green
- Emerald „
- Zinc „



• Analysed specimen

○ Date of Discovery